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# DENTAL METALLURGY

A

## MANUAL FOR THE USE OF DENTAL STUDENTS.

BY

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THIRD EDITION, REVISED.

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## PREFACE TO THE THIRD EDITION.

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IN the revision of this work for a third edition, the author has adopted the system of spelling and pronunciation of chemical terms as recommended by the Chemical Section of the American Association for the Advancement of Science, among the prominent features of which is the dropping of the final *e* from all words terminating in *ide*, the pronunciation being *id*, as chlorid, iodid, etc. ; and in sulphur and its compounds the spelling is changed to sulfur, sulfid, sulfite, sulfate, sulfó, etc.

The work has not been greatly enlarged, the author believing that for the present its original scope is sufficient for the needs of dental students.

The chapters on Amalgams, Aluminum, and Iron and Steel have been somewhat amplified, and made to embody the recent improvements in the production of those materials.

CHARLES J. ESSIG.

Nov. 6, 1893.

## PREFACE TO THE SECOND EDITION.

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THE practical results of the publication of the first edition of the Manual of Metallurgy, then the first text-book of the kind adapted to the use of dental students, showed that it filled a want long felt, and demonstrated the necessity for preparing a second edition. I have accordingly carefully revised the work, and while it has not been greatly enlarged, the more recent improvements in the reduction of metals and the formation of alloys and amalgams used in dentistry have been incorporated. As in the first edition, my aim has been to avoid extraneous or merely hypothetical matter, as well as that belonging to the purely chemical study of the metals, his knowledge of which it is presumed the student should derive from other sources.

The success of the first edition, in so far as it has been of service to students of dentistry, and the kindly reception accorded it by my collaborators, are subjects of peculiar gratification and grateful appreciation on my part.

CHARLES J. ESSIG.



## PREFACE TO THE FIRST EDITION.

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THE object of the author in the preparation of this Manual was to place in the hands of students of dentistry an outline of the scientific principles involved in the reduction of the metals, their properties, the modifications resulting from alloying, and their application to dental uses.

While the properties of many of the metals have been only incidentally or illustratively referred to, special consideration has been given to those most commonly used by dentists.

In Chapter V a *résumé* of the author's experiments in the formation of alloys for amalgams is given. These were made for the purpose of enabling him to present the subject systematically to the students who sat under his teachings ; and, while the chapter is far from being a complete treatise on the subject, it is hoped that it will prepare the dental student for a better comprehension of that branch of metallurgy, occupying, as it does, so conspicuous a place in the practice of dentistry.

As the atomic weights, specific gravity, and fusing-points of the metals are somewhat differently stated by various authors, the figures given in this Manual

have been made to correspond to those in Fownes's Chemistry,—the text-book commonly used by dental students.

The decimal system has been used to express proportions, in the belief that its comprehensiveness and simplicity would commend it.

In expressing temperatures the Centigrade and Fahrenheit scales have been occasionally referred to separately. The rule for translating one into the other, and comparative tables, have been omitted because they are to be found in Fownes's and nearly all the other recent works on chemistry, with some one of which the student is supposed to be more or less familiar.

C. J. E.

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## CHAPTER I.

### METALLURGY.

THE art of separating metals from their ores, or from simple combinations with non-metallic elements, and their application to useful purposes, may be regarded as a separate branch of chemical science. It is essential that the student, before commencing its study, should acquire a good preliminary knowledge of chemistry and mechanics.

The empirical reduction of the ores of metals seems to have been practiced at a very remote period, its origin being attributed to Tubal Cain, seventh only in descent from Adam.\* The remains of numerous mines have been discovered on the southern and eastern borders of the Ural Mountains, in which have been found hammers and chisels of copper, and other instruments of the same metal of which the uses at present are unknown.† That these implements were those of a wandering people would seem to be evidenced by the absence of any traces of masonry in the neighborhood; and the fact that no iron tools were found near them would indicate their great antiquity.

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\*In the fourth chapter of Genesis Tubal Cain is spoken of as an "instructor of every artificer in brass and iron."

† Percey's Metallurgy.

Gmelin found in the eastern part of Siberia the remains of nearly one thousand smelting-furnaces, very primitive in character, surrounded by heaps of scoria, broken pottery, and other evidences that metallurgical operations of considerable magnitude had been at some distant period carried on in that locality.\*

The alchemists of the Middle Ages were the metallurgists *par excellence* of that period, and there is evidence that they were acquainted with chemical processes for the reduction of metals, which were brought to a great state of perfection, thus showing that the practical part of metallurgy was far in advance of the theoretical.†

To these early experimenters, however, must be awarded the credit of great industry. They knew nothing of the metals as ultimate bodies, nor of the

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\* Percey's Metallurgy.

† The following experiments, from manuscripts discovered by M. Ferdinand Hofer, will serve to convey an adequate idea of the status of metallurgy from the third and fourth centuries down to a comparatively recent date :

" Experiment No. 1.—A piece of red-hot iron is placed under a bell, which rests in a basin full of water. The water diminishes in volume, and a candle, being introduced into the bell, sets fire at once to the gas inside. Conclusion—water changes into fire.

" Second Experiment.—A piece of lead, or any other metal except gold or silver, is burned in contact with the air. It immediately loses its primitive properties, and is transformed into a powder or species of ashes or lime. The ashes, which are the product of the death of the metal, are again taken and heated in a crucible, together with some grains of wheat, and the metal is seen rising from its ashes and reassuming its original form and properties. Conclusion—metals are destroyed by fire and revived by wheat and heat.

" Third Experiment.—Argentiferous lead is burned in cupels composed of ashes of pulverized bones; the lead disappears, and at the end of the operation there remains in the cupel a nugget of pure silver. Conclusion—lead is transformed into silver." (It is probable that upon this and analogous facts was founded the theory of the transmutation of metals.)

particular force governing their union with the non-metallic elements, and finding that an earthy matter, such as an ore of iron, became converted by fire into a metal, they naturally believed the change of earth into metals to be possible, and in the search for gold, the philosopher's stone, etc., they really, by mere accident, discovered many valuable chemical agents. In this way sulfuric, nitric, and hydrochloric acids were produced, and these, made to act upon the metals, in turn yielded the metalline salts.

Thus it will be seen that from the gradual aggregation of facts resulting from the pursuits of the alchemists ultimately sprang an exact science, and toward the latter part of the sixteenth century appeared a set of investigators of a very different order, who, instead of wasting their time in the pursuit of such fanciful theories as that of transmutation, etc., devoted themselves to the unraveling of the principles that govern the composition and forma-

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"Fourth Experiment.—A strong acid is poured on copper; the metal is acted upon, and in process of time disappears; or, rather, is transformed into a green, transparent liquid. Then a thin plate of iron is plunged into the liquid, and the copper is seen to reappear in its ordinary aspect, while the iron in its turn is dissolved. Conclusion—iron is transformed into copper."

Practically the fourth experiment, quoted from Jules Andrieu's paper on "Alchemy," written for the *Encyclopædia Britannica*, is electrolysis, the principle by which a compound of a metal with a non-metal is decomposed by galvanic electricity; but the transmutation theory was generally accepted as accounting for the phenomena noticed in this experiment, and it would seem that at least some of the savants of the period were sufficiently shrewd and unscrupulous to turn the process to profitable account, since we find that "St. Thomas Aquinas, in his theological writings, forbids the sale of 'alchemist's gold,' and in a special treatise on the subject unmasks an imposture of the charlatans of the day, who pretend to make silver by projecting a sublimate of white arsenic on copper."

tion of bodies already known. Thus, Paracelsus\* was the first to distinguish the true character of some of the well-known salts, such as alum and copperas, showing that they contained metals,—a matter of great importance at that day, inasmuch as it eventually led to the discovery that many of the well-known crystalline salts were compounds of dissimilar elements, as a metal with a non-metallic body, and to a knowledge of the particular force governing their union; and finally the investigations of Beecher and Stahl of Cronstadt, Klaproth, Wollaston, Berzelius, Wohler and Deville, and others, have dispelled many illusions and rendered accurate the present literature of the subject. During the latter half of the eighteenth century the list of metals was augmented by new discoveries, and the application of the voltaic current to the decomposition of the alkalies by Sir Humphry Davy in 1807–8 added a dozen or more. The employment of the spectroscope by Kirchhoff and Bunsen, in 1860, brought to light so many new metals that the total number now exceeds fifty.

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\*Paracelsus, though the author of many fanciful doctrines, seems to have been the first to offer a true chemical explanation of the action of mercury, lead, etc., upon the human system.



## CHAPTER II.

### THE METALLIC ELEMENTS.

MODERN CHEMISTRY assumes that the metals are elementary bodies, yet there have been other theories presented regarding their ultimate character, and it is thought by some that "when man shall have mastered that great power of nature, electricity, many of the so-called elements will be found probably to be compound bodies." Others have entertained the theory of but one ultimate element,\* while nearly all agree that as we advance in knowledge new elements will be brought to light.

The old philosophers applied the term element to imaginary principles of matter, such as fire, water, and air; while the elements of the alchemists were salt, sulfur, and mercury. The term is now used as synonymous with simple body, or one of the undecomposable constituents of any kind of matter, or that which cannot be divided by chemical analysis.

The elements known at present number sixty-seven, divided into the metallic and non-metallic. Of the former there are fifty-two, as follows :

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\* Prof. Graham's Researches with Hydrogen, in 1869.

NAMES.	SYMBOLS.	COMBINING WEIGHTS.
Aluminum.	Al.	27.4
Antimony.	Sb. ( <i>Stibium</i> )	122
Arsenic.	As.	75
Barium.	Ba.	137
Beryllium.	Be. (or <i>Glucinum.</i> )	9.4
Bismuth.	Bi.	210
Cadmium.	Cd.	112
Cæsium.	Cs.	133
Calcium.	Ca.	40
Cerium	Ce.	92
Chromium.	Cr.	52.2
Cobalt.	Co.	58.8
Copper.	Cu. ( <i>Cuprum</i> )	63.4
Davyum.	Da.	(?)
Didymium.	D.	95
Erbium	E.	168.9
Gallium.	Ga.	68
Gold.	Au. ( <i>Aurum</i> )	197
Indium.	In.	113.4
Iridium.	Ir.	198
Iron.	Fe. ( <i>Ferrum</i> )	56
Lanthanum.	La.	93.6
Lead.	Pb. ( <i>Plumbum</i> )	207
Lithium.	Li.	7
Magnesium.	Mg.	24
Manganese.	Mn.	55
Mercury.	Hg. ( <i>Hydrargyrum</i> )	200
Molybdenum.	Mo.	96
Nickel.	Ni.	58.8
Niobium.	Nb.	94
Osmium.	Os.	199.2
Palladium.	Pd.	106.6
Platinum.	Pt.	197.4
Potassium.	K. ( <i>Kalium</i> )	39.1
Rhodium.	Rh.	104.4
Rubidium.	Rb.	85.4
Ruthenium.	Ru.	104.4

NAMES.	SYMBOLS.	COMBINING WEIGHTS.
Silver.	Ag. ( <i>Argentum</i> )	108
Sodium.	Na. ( <i>Natrium</i> )	23
Strontium.	Sr.	87.6
Tantalum.	Ta.	182
Terbium.	Ter.	148.5
Thallium.	Tl.	204
Thorium.	Th.	235
Tin.	Sn. ( <i>Stannum</i> )	118
Titanium.	Ti.	50
Tungsten.	W. ( <i>Wolframium</i> )	184
Uranium.	U.	240
Vanadium.	V.	51.2
Yttrium.	Y.	92
Zinc.	Zn.	65.2
Zirconium.	Zr.	89.6

Of these, only about fifteen are employed in true metallic condition. These are :

Antimony,	Lead,
Aluminum,	Magnesium,
Bismuth,	Mercury,
Copper,	Nickel,
Gold,	Platinum,
Iridium,	Silver,
Iron,	Tin,
	Zinc.

Twelve are more or less extensively used in medicine, and in the arts as coloring pigments and for alloying purposes. These are :

Arsenic,	Lithium,
Barium,	Manganese,
Cadmium,	Potassium,
Calcium,	Sodium,
Chromium,	Titanium,
Cobalt,	Uranium.

The remaining twenty-five are as yet of little or no practical use in the metallic state.

Seven of the metals play a more or less important part in the maintenance of animal and vegetable life. These are :

Aluminum,	Manganese,
Calcium,	Potassium,
Iron,	Sodium.
Magnesium,	

The metallic elements are divided by metallurgists into two classes,—the *noble* and *base* metals. The first are those which are capable of being separated from combinations with oxygen by merely heating to redness. The base metals are those whose compounds with oxygen are not decomposable by heat alone.

The noble metals are ten in number, as follows :

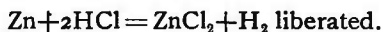
Mercury.	Hg.	200
Silver.	Ag.	108
Gold.	Au.	197
Platinum.	Pt.	197.4
Palladium.	Pd.	106.6
Rhodium.	Rh.	104.4
Ruthenium.	Ru.	104.4
Osmium.	Os.	199.2
Iridium.	Ir.	198
Davyum.	Da.	(?)

The base metals are further subdivided according to their affinity for oxygen and other chemical properties.

## CHAPTER III.

### PROPERTIES OF THE METALS.

A METAL may be defined as an elementary substance, usually solid at ordinary temperatures,\* insoluble in water, fusible by heat, and possessing a peculiar luster, commonly spoken of as a "metallic luster," an expression sometimes used in describing the appearance of substances which present a similar condition of surface. To these qualities must be added those of conducting heat and electricity, which the metals possess to the greatest extent, and the power of the metals of replacing hydrogen in chemical reactions; as, when zinc is placed in contact with hydrochloric acid, it displaces the hydrogen and unites with the chlorine to form zincchlorid (chlorid of zinc), thus:



Another characteristic of the metals is their basic properties when united with oxygen.

Arsenic and tellurium are by some regarded as intermediate links between the metallic and non-metallic bodies. Watts, in his "Dictionary of Chemistry," says of tellurium that "this element, though decidedly metallic, must be classed as a member of

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\*Mercury is an exception, being fluid at the ordinary temperature. It freezes at  $-40^{\circ}$  F.

the sulfur family," probably in consequence of its poor conducting qualities and the acid character of its oxids.

Bloxam does not regard arsenic as a metal, and states that, though "some authorities class it as such on account of its metallic luster and property of conducting electricity, yet it is lacking in the quality of forming a base with oxygen, a property common to all the true metals;" and asserts that "the chemical character and composition of its compounds connect it in the closest manner with the phosphorus group."

On the other hand, we find some of the non-metallic bodies possessing the chemical but not the physical properties of the metals. Thus, the real nature of hydrogen has long been an interesting point of discussion among chemists, some supposing it to be a metal in a gaseous form. Dumas and others prophesied that "if ever the means of liquefying hydrogen is found, it will present the appearance of quicksilver," and their grounds for this belief are its uniformly basic properties. Others contend that it is a neutral substance, possessing both the basic properties of a metal and the chlorous qualities of a gas.

In 1869 it was announced that Professor Graham, an eminent English chemist, had discovered the metallic hydrogen. "This new metal, baptized 'hydrogenium,' was white, magnetic, of a specific gravity about 2, and appeared to have some analogy to magnesium." This discovery excited much speculation. Upon verification, however, the new metal was found to be a compound of palladium and hydrogen, in which the former had absorbed 700 or 800 times its bulk of the latter.

Again, the existence of a hypothetic compound metal called ammonium, and having the constitution  $NH_4$ , has been assumed as the only method of explaining the perfect analogy that exists between the salts of ammonium and those of some of the metals, actual experiments having already strengthened this theory, at first founded only on analogy.\*

The metals are all quite opaque, with the single exception of gold, which, however, is only transparent in leaves of a highly attenuated condition, when it transmits green light.†

The *Color* of the metals ranges from the pure white of silver to the bluish hue of lead. Between these two the major part of the others may be found. About five run from light yellow to deep red. These are, barium and strontium, pale yellow; calcium, somewhat deeper in color; gold, when pure, of a rich yellow; and copper, the only red metal. It was at one time supposed that the mineral titanium, well known to dentists as a dark red (copper-colored), crystalline substance, used in a finely divided state as a coloring pigment in the manufacture of porcelain teeth, was a metal. It was so pronounced by Wollaston. Wohler and Deville, however, demonstrated that the red mineral is an oxid, and they verified their statement by producing the metal itself, which is of a steel-gray color. The color of the metals is modified by alloying.‡

*Luster.*—This characteristic of the metals is prob-

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\* E. Miller, Treatise on Chemistry.

† It is by some believed that the absence of transparency in the other metals may only depend upon our inability to obtain them in a sufficiently attenuated condition.

‡ See chapter on "Alloys."

ably the result of perfect opacity, by which the rays of light are reflected from the surface.

*Odor and Taste* are possessed by some few of the metals. The greater number, however, are destitute of these qualities. Iron, copper, and zinc, when heated, evolve peculiar odors, and one means of detection of arsenic is the odor of garlic observed when that metal is exposed to an elevated temperature. Odor and taste may depend upon voltaic action. The former may be noticed in a marked degree when holding in the hand a mass of an alloy composed of gold, platinum, tin, and silver prepared for use as amalgam. The moisture of the hand, aided by its heightened temperature, seems to promote the electrical action.

*Fusibility.*—All metals admit of being reduced to a liquid state by the application of heat, but the temperature at which they melt differs widely. Thus, mercury retains its liquid form to 39° F. below zero, and is always fluid at ordinary temperatures. Potassium and sodium fuse below the boiling-point of water; tin, lead, and antimony below redness. Gold, silver, and copper require bright redness. Iron, nickel, and cobalt fuse at white heat, while platinum, iridium, rhodium, titanium, etc., become fluid only when exposed to a powerful voltaic current or the flame of the oxyhydrogen blow-pipe.



Table of Fusing-points of the Principal Metals.

		FAHR.	CENT.
Fusible below red heat.	Mercury	-39°	-39.44°
	Rubidium	+101.3	+38.5
	Potassium	144.5	62.5
	Sodium	207.7	97.6
	Lithium	356	180
	Tin	442	227.8
	Cadmium	442	227.8
	Bismuth	497	258
	Thorium	561	294
	Lead	617	325
	Tellurium, rather less fusible than lead.		
	Arsenic, unknown.		
	Zinc	773	412
	Antimony, just below redness.		
		FAHR.	CENT.
Red heat.	Silver	1873	1023
	Copper	1996	1091
	Gold	2016	1102
Highest heat of forge.	Cast Iron	2786	1530
	Pure Iron		
	Cobalt		
	Manganese .		
Agglomerate, but do not melt in forge.	Palladium		
	Molybdenum		
	Uranium		
	Tungsten		
	Chromium		
Fusible only by oxyhydrogen blow-pipe.	Titanium		
	Cerium		
	Osmium		
	Iridium		
	Rhodium		
	Platinum		
Tantalum			

*Capacity for Heat.*—The metals, in common with other bodies, have their specific heat. This consists in the amount of heat required to raise equal weights of different metals from the same to another given temperature. Thus, if we express by 1 the quantity of heat necessary to raise a weight of water from 0° C. to 1° C., that which must be supplied to elevate the same weight of the following metals to that temperature would be as follows : \*

Mercury	0.03332
Gold .	0.03244
Iron .	0.1138
Nickel	0.1086
Cobalt	0.1070
Zinc	0.0956
Copper	0.0952
Palladium .	0.0593
Silver	0.0570
Cadmium	0.0567
Tin	0.0562
Antimony .	0.0508
Lead	0.0314
Platinum	0.0311
Bismuth	0.0308

Now, if we should take equal bulks of these metals and expose them for the same length of time to exactly the same heat, and then place them simultaneously upon a cake of wax, we would observe those of the above table with the highest figures, such as iron, instantly melting their way through the wax, while those of the lowest capacity for heat, such as bismuth, would remain on the surface.

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\* Phillips's Metallurgy, p. 13.

*Expansion by Heat.*—Metals expand when heated, but this property is not uniform, some possessing it to a greater or less extent than others. Within certain limits of temperature this takes place proportionately to the amount of heat to which they are exposed. Zinc possesses a rather high degree of expansibility, and is consequently useful for the purpose of making dies for swaging metal plates for artificial dentures. By many dentists it was formerly thought that a metal, to be well suited for this purpose, should be entirely destitute of this property, so that after casting the die should not, in returning to its former condition in cooling, be smaller than the plaster model, the object *per se* being to have the plate fit the plaster cast perfectly; whereas, the real purpose should be to make the plate fit the mouth closely, the plaster model being only a means to that end. Plaster expands in setting. From the impression to the model two expansions are gone through before the fac-simile of the mouth in plaster is obtained; hence, a plate made to fit such a model perfectly must necessarily be somewhat larger than the mouth,—a condition unfavorable to atmospheric adhesion. On the other hand, a plate made to fit the zinc will not be found too small for the mouth, but will, provided the impression is a good one and represents perfectly the conformation of the mouth, afford a very close-fitting plate. Even better results might be expected where the plate is somewhat smaller than the mouth, because such a condition would, in entire upper dentures, throw any undue pressure upon the alveolar ridge, while that portion of the plate covering the palatine arch would barely be in contact

with the tissues ; the pressure along the ridge would quickly promote absorption of the remains of the alveoli, and a uniform adaptation of the plate to the mouth would soon follow. On the contrary, if the plate be made to fit the plaster cast, and is a trifle larger than the mouth, the pressure will be thrown upon the palatine arch at the back edge of the plate, at a region not likely to change by absorption, as is the case with the alveolar ridge, and hence the margin of the plate will imbed itself in the tissues and cause much discomfort and impair the usefulness of the denture.

Much time and thought have been expended in the effort to discover some alloy which, in connection with the properties of hardness and fusibility, shall possess that of non-expansibility when heated. Harris's "Principles and Practice of Dentistry" gives no less than nine different formulæ. The author is satisfied that the property of expansibility in zinc as used in the dental laboratory constitutes one of its most valuable qualities, as it gives us the means of compensating for the yielding of the tissues and the absorption along the ridge which nearly always follows the first insertion of an artificial denture.

Table of Expansion of Metals for each degree from 0° C. to 100° C.\*

Gold	0.00155155	Lead	0.00284836
Silver	0.00190868	Tin .	0.00193765
Platinum .	0.00099180	Zinc (cast)	0.00294167
Palladium	0.00100000	“ (ham'r'd).	0.00310833
Copper	0.00171733	Bismuth	0.00139167
Iron	0.00123504	Antimony	0.00108333

\* Phillips's Metallurgy.

*Power of Conducting Heat.*—The metals are the best conductors of heat among the solid bodies. The quality of transmitting heat is possessed by them in variable degrees. The following table shows the relative approximate ratio of conductivity of heat of each of the metals commonly used in the mechanic arts :

Silver	100
Copper	73.6
Gold	53.2
Brass*	23.6
Tin .	14.5
Iron	11.9
Steel	11.6
Lead	8.5
Platinum	8.4
German Silver	6.3
Rose Fusible Metal	2.8
Bismuth	1.8

*Power of Conducting Electricity.*—Metals conduct electricity nearly in the ratio of their capacity of transmitting heat. Davy, Becquerel, and Dr. Matthiesen have, at different times, more or less extensively experimented upon this characteristic quality of the metals. Among the results of Dr. Matthiesen's investigations are the facts that debasing a metal or alloying it greatly diminishes its conducting power, and that elevation of temperature has the same effect, and that between 32° and 212° F (or 0° and 100° C.), great diminution takes place,—not uniformly, however, as some lose it more in proportion than others. †

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\* Zinc is probably between brass and tin.

† Makins's Metallurgy, p. 17.

A rough means of determining the relative conducting power of metals consists in connecting the poles of a voltaic battery by a wire through which the current will pass freely. Now, if the wire be too small for the transmission of the electricity supplied to it, the obstruction will be manifested by the wire becoming red-hot.\*

Hence the relative capacity of metals for this purpose may be observed by employing equal battery-power upon wires of the same diameter of different metals, and noting the length of the portion of each which can thus be heated.

Conversely, the same means may be employed to indicate the quantity of electricity, or the capacity of the battery itself. In this case the wire is made to demonstrate the power of the battery by the length of wire which the battery is capable of rendering incandescent.

A good demonstration of the relative conducting power of different metals may be made by constructing a chain of alternate links of platinum and silver wire. This will show, while the current of electricity is passing, red-hot platinum links alternating with cool silver ones. Platinum, being much the inferior conductor, offers such an impediment to the passage of the current that great elevation of temperature results, while the silver, being a good conductor, offers no check to the free passage of the electricity.

The power of metals of conducting electricity is

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\*This was fully shown in some of the early experiments with the electro-magnetic mallet, in which the wire was too small for the accompanying battery power. They worked very well for a few minutes, when they became hot and ceased working.

shown in the following table from Matthiesen (Phil. Trans. 1863) :

Silver	100	at 32° F.
Copper.	99.95	“ “
Gold	77.96	“ “
Zinc	29.02	“ “
Iron	16.81	“ “
Tin	12.36	“ “
Lead	8.32	“ “
Antimony	4.62	“ “
Bismuth	1.24	“ “

*Malleability, Ductility, and Tenacity.*—The qualities of malleability, ductility, and tenacity differ widely in the metals. The term *Malleability*, when applied to such a metal as gold, signifies that by hammering or rolling its surface may be extended in all directions, and that it is capable of being thus reduced to very thin leaves or sheets without fracture of its continuity at the edges during the process of attenuation ; when applied to other metals, the term should be understood as expressing this quality relatively. Gold is the most malleable of the metals, and is capable of being made into leaves of  $\frac{1}{800000}$  of an inch in thickness, each grain of which will cover a surface of 54 sq. inches.

In the following list, by Regnault,\* the metals are arranged in the order of their malleability :

- |             |              |                       |
|-------------|--------------|-----------------------|
| 1. Gold.    | 6. Platinum. | 11. Palladium.        |
| 2. Silver.  | 7. Lead.     | 12. Potassium.        |
| 3. Tin.     | 8. Zinc.     | 13. Sodium.           |
| 4. Copper.  | 9. Iron.     | 14. Mercury (frozen). |
| 5. Cadmium. | 10. Nickel.  |                       |

*Ductility* signifies that property which renders a

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\* Phillips's Metallurgy, p. 412.

metal capable of being drawn into rods or wires, usually accomplished by passing an elongated piece of metal through a series of gradually diminishing holes in a steel draw-plate; the granular particles of the metal are thus extended into fibers. One grain of gold has been drawn into a wire 550 feet long. To accomplish this result a compound wire is made, of gold covered with silver, the tenacity of the latter being taken advantage of to enable the gold to be carried through the successive holes of the draw-plate, until the greatest possible attenuation is reached; after which it is immersed in nitric acid, which dissolves the silver, leaving a gold wire  $\frac{1}{5000}$  of an inch in diameter.

In the following table the metals are arranged according to their ductility :

1. Gold.	5. Copper.	9. Nickel.
2. Silver.	6. Zinc.	10. Palladium.
3. Platinum.	7. Tin.	11. Cadmium.
4. Iron.	8. Lead.	

*Tenacity* is the power possessed by metals of sustaining weight, or of resisting rupture, when a bar or rod is exposed to tension. As the fitness of metals for certain purposes in the industrial arts depends largely upon this property, it is of the utmost importance to know the relative tenacity, not only of the different metals, but of different alloys. This is usually ascertained by preparing wires of exactly equal diameters. These are suspended by one end from a fixed bar, and to the other extremity weights are gradually and carefully added until the wire breaks. The weight which causes the fracture rep-



resents, when compared with other wires similarly treated, the relative tenacity of the metal.

Elevation of temperature, even within rather circumscribed limits, affects the tenacity of metals to a marked degree, generally *diminishing* it. There are some exceptions, such as iron and steel. On the other hand, malleability and ductility are only developed in some of the metals by an elevated temperature. Thus, it was found that zinc, which had previously been of no use in an unalloyed state, was rendered perfectly malleable and capable of being rolled into very thin sheets merely by heating to between 248° and 302° F. (=120° and 150° C.), and it has consequently come very largely into use. If carried much beyond this point, however, say to 400° F. (=205° C.), it becomes very brittle, and may even be reduced to powder in an iron mortar. A rather unsatisfactory demonstration of this fact sometimes occurs in the fracture incident to the falling upon the hearth or floor of a hot zinc die, carelessly removed from the molding sand in the laboratory, its brittleness being so extreme at 500° F. that it might be broken into a number of pieces.

Magnesium, aluminum, and some other metals, which at ordinary temperatures are nearly destitute of ductility, have that quality greatly increased by heating, and are then readily drawn into wire.

In alloys these qualities are diminished by heating. Thus, the great tenacity and ductility of brass are entirely destroyed by simply heating to dull redness. Again, while it is claimed that in pure gold tenacity is increased by heating, it is quite certain that 18-carat gold is rendered brittle at red heat.

The following table\* gives the results of experiments on the tensile strength of a few of the metals at temperatures between 15° and 20° C.

NAME OF METAL.	For wire of 1 Sq. MM. Section, Weight (in Kilos) causing	
	Permanent Elonga- tion of 1-20,000.	Breakage.
Gold, drawn	13.5	27
“ annealed .	3.0	10
Silver, drawn	11.3	29
“ annealed .	2.6	16
Platinum, drawn	26	37
“ annealed	14	23
Copper, drawn	12	40
“ annealed	under 3	30
Iron, drawn	32	61
“ annealed	under 5	47
Palladium, drawn	18	37
“ annealed	under 5	27

The following table shows the order of relative capacity of the metals for sustaining weight :

- |              |            |          |
|--------------|------------|----------|
| 1. Iron.     | 4. Silver. | 7. Tin.  |
| 2. Copper.   | 5. Gold.   | 8. Lead. |
| 3. Platinum. | 6. Zinc.   |          |

It has been observed that students and others very often fail at first to appreciate the difference between these properties, and they not infrequently fall into the mistaken idea that the three qualities of malleability, ductility, and tenacity are possessed to an equal extent by each metal. If, however, we take gold, for example, the most perfectly malleable and

\* Annales de Chimie et de Physique (iii), vol. xii, Wertheim.

ductile of the metals, we shall find that in tenacity it ranks considerably below some of the others, and the greatest care is necessary in drawing a piece of pure gold into even a moderately fine wire, and beyond a certain limit, past which platinum or copper may be carried with safety, gold would not possess sufficient tenacity to overcome the resistance to which it would be exposed in passing through the smaller holes of the draw-plate, and fracture would result.

Iron, on the other hand, which exceeds all the other metals in tenacity, is in malleability inferior to gold, silver, copper, platinum, lead, zinc, tin, and cadmium.

Crystalline metals, such as bismuth, antimony, and arsenic, do not possess these properties. They are easily broken by even slight blows of a hammer, and the two latter may be reduced to powder in a mortar.

It is stated that brass drawn into wire will often, after a time, become crystalline in texture and brittle by slow change of molecular arrangement.\*

*Crystallization.*—It is stated that under favorable circumstances all the metals will assume a crystalline form. It is known that some of them, as gold, silver, etc., are found native as cubes or octahedra, or in slight modifications of these forms; and metals in a crystalline form may be obtained by electrolysis. For example, silver may be obtained in the form of crystals nearly pure by introducing strips of copper into a solution of argentic nitrate. A piece of zinc introduced into a solution of plumbic nitrate will precipitate the lead in the form of feathery crystals. Gold may also be deposited in this form from solution by the introduction of a stick of phosphorus. Nearly

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\* Makins's Metallurgy, p. 10.

all the metals yield crystals when deposited from their solutions by electric currents of feeble intensity. The beautiful preparation known as Watts's Crystal Gold is formed in this way. Gold so prepared is generally in a high state of purity.

*Elasticity* and *Sonorousness* may be conferred upon the metals by alloying. Thus, iron does not possess these qualities until combined with the proper proportions of carbon, when by subsequent tempering the highest degree of elasticity is developed, and pieces of steel of different lengths, as arranged in the dulcimer, when struck by a small wooden hammer, are capable of giving off the most musical sounds.

Again, a very great amount of elasticity is obtained by the admixture of copper and zinc in the form of brass, from which a spiral spring may be made, equal to that from any other alloy.

It is curious to observe how this quality may be developed by the admixture of two metals, each of which, examined separately, is soft and destitute of anything like springiness. Thus, gold and platinum, both soft metals, when combined in the proportions of, say, 1 grain of the latter to 1 dwt. of the former, of 20-carat fineness, will afford a decidedly elastic alloy, suitable for clasps for artificial dentures.

A tolerably elastic alloy may be formed by combining platinum with a small amount of iridium. This alloy is frequently employed in the construction of artificial dentures.\*

Sonorousness is obtained to the greatest extent in alloys of copper and tin, known as bell-metal.

*Volatility*.—All metals are probably more or less

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\* See chapter on "Platinum and its Alloys."

volatile, although only a certain number admit of being converted with any degree of facility into a state of vapor, even at the highest temperatures. Some of the conspicuously volatile metals are zinc, cadmium, mercury, arsenic, tellurium, potassium, and sodium; while a few others have the property of communicating characteristic colors to flame, and are probably volatile to a limited extent.

Metals are sometimes characterized as "fixed," as gold, copper, nickel, etc., and "volatile" (during fusion), as cadmium, zinc, etc. Arsenic may unquestionably be regarded as belonging to the latter group, passing as it does without fusion from the solid to the gaseous state.

Gold has been known to volatilize under certain conditions. Makins states that it is doubtful whether it is at all volatile *per se*, but if alloyed with copper it has been shown by Napier to be considerably volatilized, so that quantities amounting to  $4\frac{1}{2}$  grains could be collected during the pouring of 30 pounds' weight from a crucible. According to Makins, gold has been known to volatilize when mixed with silver and lead and cupelled together, he having collected considerable quantities of each metal from the chimney of an assay furnace after only a few weeks' use.

*Agents which may Volatilize a Metal.*—Concentration of solar rays in the focus of a lens; the voltaic current; the oxyhydrogen blow-pipe flame.

M. Despretz employed the three in conjunction, by which means he volatilized magnesium, and with a powerful Bunsen battery alone he reduced carbon by volatilization to the state of a black powder.\*

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\* Percey's Metallurgy.

## CHAPTER IV.

### ALLOYS.

**M**OST of the metals are capable of uniting with one another, forming a class of compounds termed alloys, in which may be observed to a greater or less extent the properties of the several constituents entering into the union.

From a purely scientific point of view, the study of the alloys is an interesting one, as they are not only mixtures of metals possessing certain distinct qualities, but in reality are true chemical compounds. In the appearance which often accompanies the union of the metals, and in the properties of the resulting alloys, we may frequently observe the phenomena which characterize chemical affinity, such as heat and incandescence, resulting in the formation of substances having a definite composition, distinct crystalline form, and properties differing from those of their constituents.

When a piece of clean sodium is rubbed in a mortar with dry mercury, the former dissolves, and a peculiar seething sound, resembling that caused by the immersion of a hot body in water, is produced, due to the evolution of heat which accompanies the combination, the mercury rising rapidly in temperature as the pieces of sodium are added. As the mercury

cools, the resulting alloy, which is brilliantly white, crystallizes in long, needle-like forms from the middle of the liquid, and the excess of mercury may be poured off.

Alloys are generally harder and more fusible than the metals of which they are formed, and as many metals are unfit in the pure state for use in the mechanic arts, owing to extreme softness or high fusing-point, these properties are modified to suit various requirements by the admixture of other metals. Thus, as a base for an artificial denture, pure gold would be too soft to withstand, without bending, the force to which the fixture would be exposed during mastication, but by the addition of sufficient copper and silver to reduce the gold to .750 (18 carats) the necessary rigidity may be obtained without materially affecting the other properties. Again, it is often desirable to unite several pieces of the same metal or of different metals. This is accomplished by means of a class of alloys called solders, generally formed of the metal upon which they are to be employed with the addition of some other metal which will considerably lower the fusing-point without affecting the color, as it is desirable that the place of union should not be noticeable. For example, a solder suitable for use in prosthetic dentistry should fuse at a much lower temperature than the plate upon which it is to be used. Its color should be as nearly as possible the same, and what is even more important, it should withstand the action of the fluids of the mouth nearly as well. These properties may be obtained by the addition of small quantities of silver, copper, or brass.

The value of many of the metals for industrial uses is very greatly enhanced by alloying. Thus, copper, which is unfit for casting and too tough for turning, may, by the addition of zinc, be rendered not only harder and more elastic, but the fusing-point of the resulting compound will be so much lower than that of the copper alone as to render the casting of it a matter of no great difficulty, while at the same time it will be found susceptible of being turned in the lathe with facility.

The tendency on the part of metals to unite in definite proportions may be studied in connection with platinum, iridium, gold, rhodium, ruthenium, and silver, when fused with tin. If the latter metal is in excess, after cooling a metallic ingot is obtained resembling closely the tin; but by the action of strong hydrochloric acid upon this the excess of tin may be dissolved, leaving crystals of a definite alloy of the tin and the noble metal, which cannot be further dissolved by the same acid, but are soluble in nitrohydrochloric acid, even when the precious metal contained, whether rhodium, ruthenium, or iridium, is in the free state absolutely insoluble by that agent.

It must not, however, be assumed that all the alloys employed in the industrial arts are the result of definite combination dissolved in an excess of one of the metals. Many combinations are capable of co-existing in the same alloy. This may be demonstrated in an alloy of tin, lead, and bismuth, which melts below the boiling-point of water. Heated to  $25^{\circ}$  C., and then permitted to cool, it will be observed, by the assistance of the thermometer, that the fall of temperature is twice distinctly arrested. The cause of



this phenomenon has been assumed to be the production in the compound of a less fusible alloy, which in solidifying evolves heat, and thus for a time retards the gradual cooling of the mass. It may, therefore, be assumed that true chemical combinations may occur between two metals, notwithstanding the fact that such union may be masked by excess of one of the constituents.

Matthiesen, in an elaborate paper on the subject, states that "an alloy may be, first, a solidified solution of one metal in another; second, a chemical combination; third, a mechanical mixture; or fourth, a solidified solution or mechanical mixture of two or all of the above." In simple mechanical mixture of two metals there is often a tendency to separate. This is noticeable in some alloys of silver and copper by an absence of perfect homogeneity in the ingot. Again, some of the metals form mixtures so decidedly mechanical that on being allowed to stand after fusing they will separate, the one possessing the highest specific gravity settling to the bottom. This may be observed when lead and zinc are mixed. Matthiesen, however, found that the lead retains 1.6 per cent. of the zinc, while the zinc retains 1.2 per cent. of the lead.\*

*Density.*—Theoretically, it might be supposed that the density of an alloy would be the mean of its constituents. Such, however, is not always the case, as the resulting number is sometimes equal to, or greater or less than, the theoretical mean. The density of alloys of gold and silver is less than the mean of the components, in consequence of expansion; while brass and alloys of lead and antimony vary in the opposite

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\* Makins's Metallurgy, p. 62.

direction, through a condensation of their constituents. But in the formation of some alloys there is no alteration of volume, and the density of such will correspond to that obtained by calculation as the mean of their constituents.

The following table,\* by Thénard, gives examples of variations of density in alloys :†

Alloys possessing a Greater Specific Gravity than the Mean of their Components.	Alloys having a Specific Gravity Inferior to the Mean of their Components.
Gold and Zinc.	Gold and Silver.
“ “ Tin.	“ “ Iron.
“ “ Bismuth.	“ “ Lead.
“ “ Antimony.	“ “ Copper.
“ “ Cobalt.	“ “ Iridium.
Silver and Zinc.	“ “ Nickel.
“ “ Lead.	Silver and Copper.
“ “ Tin.	Copper and Lead.
“ “ Bismuth.	Iron and Bismuth.
“ “ Antimony.	“ “ Antimony.
Copper and Zinc.	“ “ Lead.
“ “ Tin.	Tin and Lead.
“ “ Palladium.	“ “ Palladium.
“ “ Bismuth.	“ “ Antimony.
“ “ Antimony.	Nickel and Arsenic.
Lead and Bismuth.	Zinc and Antimony.
“ “ Antimony.	
Platinum and Molybdenum.	
Palladium and Bismuth.	

*Color* is always modified by alloying. It is generally such as might be expected to result from the mixture of the metals entering into the formation of

\*Phillips states that it is doubtful whether some of the mixtures included in this table should be regarded as alloys.

† Phillips's Metallurgy.

the alloy. There are a few instances, however, where it is different. Thus, three parts of silver to seven of gold yields a green alloy, and nickel, added to brass, produces an alloy of silvery whiteness.

*Malleability, Ductility, and Tenacity.*—These properties are generally much changed in metals by alloying; malleability and ductility being diminished, and in some cases entirely destroyed, even in the combination of two very ductile metals, as is the case with gold containing a small quantity of lead, ductility being completely lost. Again, gold and platinum, two exceedingly ductile metals, are rendered much harder and somewhat elastic by admixture.

The union of a brittle and a ductile metal yields a brittle alloy. According to Mr. Makins, antimony, a metal so brittle that it may be broken up in a mortar, when added to gold to the extent of  $\frac{1}{1900}$  part, will make the gold quite unworkable.

Tenacity is generally increased by alloying. The following results were obtained by Matthiesen, by employing wires of the same gauge and noting the weights which caused their rupture before and after alloying:

	LBS.		LBS.
Copper, unalloyed,	25 to 30;	alloyed with 12 per ct. Tin,	80 to 90
Tin,	“ under 7;	“ “ “	Copper, 7
Lead,	“ “ 7;	“ “ Tin	7
Gold,	“ 20 to 25;	“ “ Copper	70
Silver,	“ 45 to 50;	“ “ Platinum	. 75 to 80
Platinum,	“ 45 to 50;		
Iron,	“ 80 to 90;	Steel (Iron alloyed with Carbon)	above 200

Generally speaking, the hardness of metals is increased by alloying them. A familiar instance is

standard gold or silver. Neither of these when unalloyed is sufficiently hard to resist attrition to the degree required for currency ; but the addition of one-tenth of its weight of copper to either metal increases its hardness to the required point. Ninety-four parts of copper with six parts of tin form an alloy so brittle that it may be broken with a hammer.

*Fusibility.*—The fusing-point of an alloy is always lower than that of the least fusible metal entering into the composition of the alloy. Thus, an alloy composed of five parts of bismuth, three of lead, and two of tin, melts at  $91^{\circ}$  C., less than the boiling-point of water, while tin alone fuses at  $227.8^{\circ}$  C., and lead at  $325^{\circ}$  C., and the addition of a small amount of cadmium to the above alloy will further reduce the fusing-point to  $140^{\circ}$  F., or  $60^{\circ}$  C. Lead combined with a small portion of silver is more fusible than the former in a state of purity, and an alloy may be formed of potassium and sodium, which remains fluid at ordinary temperatures of the air.

This phenomenon has been explained by Matthiessen. He says that "matter in the solid state exhibits excess of attraction over repulsion, while in the liquid state these forces are balanced, and in the gaseous state repulsion predominates over attraction, and similar particles of matter attract each other more powerfully than dissimilar particles do. The attraction subsisting between the particles of a mixture will be sooner overcome by repulsion than will the attraction in the case of a homogeneous body ; hence mixtures should fuse more readily than their constituents."\*

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\* Makins's Metallurgy, p. 65.

*Composition of Alloys.*—A statement of the average proportions in which metals enter into the best-known alloys, the composition of which is generally very variable, is given in the following table :

Coinage of Gold ..	{ Gold	90
	{ Copper	10
Gold Jewelry and Plate	{ Gold	75 to 92
	{ Copper	25 to 8
Silver Coinage	{ Silver	90
	{ Copper	10
Silver Vessels	{ Silver	95
	{ Copper	5
Silver Jewelry	{ Silver	80
	{ Copper	20
Aluminum-Bronze	{ Copper	90 to 95
	{ Aluminum	10 to 5
Specula of Telescopes	{ Copper	67
	{ Tin	33
Pinchbeck	{ Copper	90
	{ Zinc	10
Brass	{ Copper	67 to 72
	{ Zinc	28 to 33
German Silver	{ Copper	50
	{ Zinc	25
	{ Nickel	25
Type-metal	{ Lead	80
	{ Antimony	20
Bronze Coins and Medals	{ Copper	94 to 96
	{ Tin	4 to 6
	{ Zinc	1 to 5
Bronze Cannon	{ Copper	90
	{ Tin	10
Bronze Bells	{ Copper	78
	{ Tin	22
Bronze Cymbals	{ Copper	80
	{ Tin	20

English Metal	{	Tin	87
		Antimony	8
		Bismuth .	1
		Copper	4
Pewter	{	Tin	92
		Lead	8
Liquid Measures.	{	Tin	82
		Lead	18
Plumbers' Solder	{	Tin	67
		Lead	33

Alloys used as plates for artificial dentures and those constituting solders will be described with the metals forming their bases.

*Decomposition.*—When the alloy contains a volatile metal, like zinc or mercury, heat decomposes it, but the temperature required to expel the last trace of the volatile metal must be considerably higher than that metal's normal temperature of ebullition. If the alloy is composed of a noble metal and zinc, lead, or tin, and it is desired to free it from the impurity, this may be accomplished by exposure to a high temperature, and the addition, while the metal is fluid, of some substance rich in oxygen, such as potassium nitrate. By this means the base metal is converted into an oxid, and is then dissolved and held in solution by the borax, which should be used as a flux in the crucible. Metals in combination with mercury may be separated by the application of heat, the mercury volatilizing at 600° F. In the case of particles of amalgam, however, the temperature to which the pieces are exposed should be at least a bright-red heat.

*Influence of Constituent Metals.*—Mercury, bismuth, tin, and cadmium give fusibility to alloys into which they enter ; tin also gives hardness and tenacity ; lead

and iron give hardness ; arsenic and antimony render alloys brittle.

It has been observed that phosphorus and arsenic, when added to alloys of copper and tin, have the power of deoxidizing or eliminating metallic oxids, which are invariably present. The well-known phosphor-bronze owes its closeness of grain and superior tenacity to the addition of phosphorus, and it is claimed that "when arsenic or arsenical compounds are made to unite, under suitable conditions, with alloys of copper and tin, known as bronze or gun-metal, it imparts to them several remarkable and, for many purposes in the arts, desirable properties,—among others and principal of which are homogeneity, hardness, elasticity, greatly increased tensile strength and toughness, and a peculiar smoothness, rendering it a valuable anti-friction metal for journal-bearings," etc.

The arsenical compounds of alloys of copper and tin are also more fluid when molten than are other known alloys of copper and tin,—a property which renders them capable of filling out sharply and without flaws the most intricate molds.

*Liquation.*—The constituents of an alloy heated gradually to near its point of fusion frequently unite to form new compounds, and if the fluid portion is poured off, there remains a solid alloy less fusible than the original. Copper is separated from silver by this process. In bars of silver alloyed with copper, a curious tendency on the part of the latter to separate and aggregate at the edges, as the fused mass assumes the solid form, has been observed. Mr. Makins states that, as a result of careful examination of Mexican dollars and crown pieces, he found the variation

between the center and edges to range in the former from one to six, and in the latter from one to four milligrammes. He gives as the average of a number of experiments on twenty-four crown pieces a mean variation of two milligrammes, and as the quality in which the greatest tendency to separate is shown that of 900 parts of silver to 100 of copper.\*

*Temper.*—Modified conditions of hardness and elasticity of a metal, it has been shown, may be obtained by admixture with other metals and by sudden variations of temperature, as in the case of the alloy of 94 parts of copper and 6 of tin, which forms a bronze so brittle that it may, when heated and slowly cooled, be pulverized with a hammer; but if, on the contrary, it is cooled rapidly, by immersion in cold water, it becomes malleable. The treatment of iron mixed with carbon (steel) is just the opposite, the greatest degree of hardness being attained by suddenly cooling the heated mass.

*Preparation.*—When the alloy is to be formed of a noble and one or more of the base metals, the former should be thoroughly fused first; the latter is then added, and the whole covered with charcoal, to prevent oxidation, and then thoroughly mixed by stirring or agitating.

When it is designed to lower the fusing-point of gold or silver for use as solders, by the addition of brass, etc., the precious metal should first be thoroughly fused with a sufficient quantity of borax; the brass, in the convenient form of wire, should then be quickly thrust into the melted gold or silver. It will almost instantly mix with the melted mass, and

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\* Makins's Metallurgy, pp. 379, 380.



the borax, if in sufficient quantity, will cover the liquid alloy, and thus protect from oxidation by contact with the atmosphere.

The action of acids upon alloys is generally more energetic than upon a simple metal, but it varies according to the relative amounts of their constituents. Silver alloyed with a large proportion of gold is protected from the action of nitric acid. Sometimes, however, the reverse of this is seen, and metals which are totally insoluble in certain menstrua are made to dissolve in them by the addition of a metal on which they have the power of acting. Thus, platinum, although of itself insoluble in nitric acid, may be dissolved by it when sufficiently alloyed with silver.

Alloys consisting of two metals, one readily oxidizable, the other possessing less affinity for oxygen, may be readily decomposed by the combined action of heat and air. In this case the former metal will be rapidly converted into an oxid, excepting perhaps the last portions, which may in some degree be protected from further action by the oxid already formed. This increased affinity for oxygen exhibited by alloys is probably an electrical phenomenon, the study of which belongs rather to the science of chemistry than to metallurgy. For further light on this subject the student may refer to Fownes's, Bloxam's, or other standard works on chemistry.

## CHAPTER V.

### AMALGAMS.

**A**MALGAM—the name given to an alloy of mercury with one or more other metals. The amalgams are a very numerous class of compounds, and many of them are used largely in the arts.

Some amalgamations are formed merely by contact of the metals, and are accompanied by evolution of heat; others are obtained by the action of mercury on a salt of the metal, or the action of the metal on a salt of mercury, thus developing in some cases a weak electric current.

The constituents of amalgam compounds are not generally held together by strong affinities, hence many of them may be decomposed by pressure, and all by high temperatures. Tin amalgam is used for “silvering” mirrors; gold and silver amalgams in gilding and silvering; while amalgams containing gold, silver, tin, platinum, and, in some cases, cadmium, zinc, copper, and other of the base metals, compounded according to many different formulæ, have been used very extensively in dentistry. An amalgam of zinc and tin is employed for the rubbers of electrical machines.

An alloy for dental amalgams should possess the qualities of strength and sharpness of edge, and

freedom from admixture with any metal favorable to the formation of soluble salts of an injurious character in the mouth. It should be capable of maintaining its color, although in an alloy composed of several different metals absolute freedom from discoloration, under the conditions to which an amalgam filling is exposed, cannot readily be obtained. It should also be capable of retaining its shape, as the tendency on the part of many amalgams to assume a globular form after their introduction, thus leaving the edges of the cavity unprotected, is probably a frequent cause of failure in this class of fillings.

Undue expansion, although not so likely to occur as some other changes, would be equally a source of failure. According to Mr. Fletcher, amalgams of silver and mercury expand, sometimes sufficiently to split a tooth; and Mr. Kirby states that "amalgams of pure silver, either the precipitate or filings, expand greatly." With a suitable instrument for measurement, he was able to determine the change in bulk of such an amalgam, in which he found the extent of expansion to reach one-fortieth of its diameter.

Many old amalgam fillings have the appearance of projecting from the edges of the cavity as though there existed some force behind or beneath sufficient to push them out. There seems to be some diversity of opinion respecting the cause of this, and while by some it is attributed to expansion, others believe it to be due to contraction. Favoring the latter theory, Mr. Fletcher states that he has found it to occur only with those amalgams which are known to shrink, and he suggests that the plug may be raised or forced out by the "decomposition of tooth-substance and the

formation of gas under the loosened plug, the driving down and accumulation of food underneath, or some similar cause." It is evident that an amalgam liable to contract or expand to a marked extent is not to be relied upon as a filling-material.

Discoloration of dental amalgams depends largely upon the formation of sulfids. The fluids of the mouth, in every case where the most scrupulous cleanliness is not observed, may be said to contain sulfur in combination with hydrogen, as dihydric sulfid ( $H_2S$ ), resulting from decomposition of particles of food having a lodgment between or adhering to the teeth. The affinity of sulfur for both silver and mercury is so active that we may reasonably assume that not only the discoloration of amalgam fillings, but in many cases their failure to prevent a recurrence of decay, is due to the action of that element upon the alloy. Nor is it safe, in compounding alloys for dental amalgams, to depend upon the protecting influence of metals which do not possess the same affinities, such as gold and platinum; for while these metals individually may remain wholly unaffected by contact with sulfur, it does not necessarily follow that their presence in an alloy will secure the same immunity to such metals as silver and mercury.

There are doubtless other causes for the discoloration of amalgams, some of them purely adventitious, depending upon the administration of certain remedies in diseased, abnormal conditions of the fluids of the mouth, or the presence of vegetable acids in articles of food, such as fruit.

An amalgam filling may retain its integrity of

surface, while, at the same time, the darkening of the tooth-substance unmistakably indicates chemical action at its peripheral portion, doubtless due to imperfect adaptation, favoring the ingress of the eroding agent. It appears that almost any amalgam filling may be kept bright by friction, whether of the brush or from mastication, and it seems equally certain that all such fillings will blacken if the position which they occupy protects them entirely from friction. Again, an amalgam filling may retain its original color and brightness of surface, and yet not protect the tooth; and, conversely, a filling of this class may exhibit a great degree of surface-discoloration and yet fully preserve the tooth from further decay, peripheral discoloration being much the worse condition of the two.

In a number of experiments made with some of the well-known amalgams, such as Townsend's, Arrington's, "Standard Alloy," Lawrence's, Walker's, etc., as well as with some of higher grades, it was found that with care in using the proper quantity of mercury, and in packing the mass into clean glass tubes, subsequently filled with colored fluid and closely sealed, there was after several weeks not the slightest apparent leakage; and yet, when the same tubes were thrown into a solution of sulfuretted hydrogen, the edges were attacked, and marked discoloration occurred at the periphery of the fillings, while the surface directly exposed to the action of the sulfur, and not in contact with the glass, was but slightly clouded. The edges had the appearance of having been eroded, as by an acid. This experiment is not merely speculative, as it is simply filling a

cavity with amalgam and then exposing it to sulfur in the form usually found in the mouth. The result is precisely similar to that which is observed in the great majority of amalgam fillings in actual service. It would seem, however, that the purely theoretical test of covering the plug with colored fluids, such as indigo, blue ink, etc., known as the "color-test," is not to be relied upon in testing peripheral adaptation, for all the plugs used in these experiments had apparently excluded the passage of a solution of indigo or ink. Yet, that they did not perfectly seal the tubes, although introduced under very favorable conditions, was plainly shown by the result, which indicated that solutions of one or more of the constituents of the alloy had taken place, accompanied doubtless with the formation of new compounds, consisting of sulfids of silver and mercury, and in some instances, probably, of copper.

*Influence of Different Metals in Dental Alloys.*— Tin dissolves very easily in mercury, but the alloy hardens slowly and imperfectly. Without admixture with other metals it is unfit for use in the form of an amalgam in the mouth. It is also well known to possess a tendency to draw away from the edges of any cavity into which it may be packed, and to assume a globular form, and it never becomes sufficiently hard to answer the requirements of a filling-material. Mixed with other metals, tin serves to facilitate amalgamation and to afford different degrees of plasticity. Between mercury and silver the affinity is but slight. By the addition of tin, however, union is facilitated.

Silver apparently unites very readily with mercury.

Yet it will be found, upon close examination, that complete solution of pure silver filings will not take place until after long contact, unless the silver is in a finely divided state and the mercury heated. Under these circumstances, amalgamation will be more readily accomplished. Amalgams of silver and mercury alone are said to expand.

Silver with tin added forms an alloy very white in appearance, but more easily oxidized than either of the constituents; mixed with mercury, an exceedingly unctuous and plastic amalgam is obtained, but it is somewhat slow in hardening. There is much diversity of opinion in regard to the contraction and expansion of this alloy. Dr. Hitchcock and Mr. Tomes both claim contraction\* for it, while Mr. Kirby states that an "amalgam of an alloy of 3 parts of silver and 2 of tin contracts slightly at first, but finally expands about  $\frac{1}{500}$ ."† These variable results may depend upon the quantity of mercury employed. The author is satisfied that when an alloy of silver and tin is used no excess of mercury should be present, and when this precaution has been carefully observed he has found the results to be quite as good as those obtained with the alloys of the higher grades. Thus, 500 milligrammes‡ of Arrington's amalgam, composed§ of silver 40 per cent., tin 60 per cent., mixed with 160 milligrammes of mercury, withstood the sul-

\* Transactions New York Odontological Society, 1874.

† Ibid.

‡ The author has used the metric system of weights in recording his own experiments. Where data have been obtained from others, he has used the figures furnished by them, and in quoting other authorities he has not felt at liberty to change the text in any way.

§ Hitchcock, Trans. N. Y. Odont. Soc., 1874.

furetted hydrogen test quite as well as those containing gold and platinum. It should be borne in mind that alloys composed of tin and silver require much less mercury to render them plastic than those containing gold and platinum in addition.

Probably the most unfavorable property observed in an alloy of silver and tin is slowness in hardening, which favors the ingress of fluids by capillary force. The direct influence which silver exerts upon an amalgam of tin and mercury is to lessen the tendency to assume the spheroidal form, and to facilitate setting. In this respect its action is similar to that of gold; but while the latter further lessens these injurious tendencies, and confers similar properties, it cannot be made to supersede silver. In my experiments with these curious compounds I formed an alloy consisting of

Gold	500 milligrammes
Platinum	500     "
Silver	2000    "
Tin	2500    "

An amalgam of this alloy hardened almost instantly, so that a filling of it might be inserted and finished at one sitting. For the sake of experiment, another ingot was made, from which the silver was omitted. The result was an exceedingly brittle alloy, which could only be made to unite with mercury by heating, and even then with difficulty, and it did not harden *sufficiently* to be of any use as a filling-material. Thus it will be seen that silver fills an important place in dental alloys, since without its presence amalgamation becomes difficult, and rapidity in hardening is not secured.



Gold combines with mercury at all temperatures, but for rapid amalgamation an elevation of temperature is required, and the process is accelerated if the gold is in a state of fine division. With mercury alone it does not harden well; added to tin, it to a certain extent facilitates setting, but does not harden sufficiently for use in the mouth, though it prevents the tendency to draw away from the edges. But it is when added to an alloy of tin and silver that the greatest benefit is derived from its presence. I found that an alloy consisting of

Gold .	500 milligrammes,
Silver	2000 "
Tin	2500 "

when mixed with mercury in the proportion of 500 milligrammes of the alloy to 250 milligrammes of mercury, retained its sharpness of edge, hardened well in a few minutes, and apparently filled all the requirements of a dental amalgam. The author is aware of the statement which has been made that gold added to an alloy of tin and silver retards hardening, but this is doubtless an error, and the presence of an excess of mercury is the real cause of the tardiness in setting.

Platinum, in the usual form of plate or wire, does not readily unite with mercury. A very smooth and plastic amalgam may, however, be formed by rubbing some finely-divided platinum, such as is obtained by precipitation, with mercury in a heated mortar.

An amalgam composed of platinum and mercury alone does not harden well. The properties of an alloy of tin and silver are also greatly impaired by the addition of platinum in any considerable quantity.

The author found an alloy consisting of tin 2500 milligrammes, platinum 500 milligrammes, to be exceedingly brittle, and with so little affinity for mercury that amalgamation was only accomplished by elevation of temperature and much rubbing, while the property of setting was almost entirely lost.

If platinum be added to an alloy of gold and tin, the same negative results are observed. When combined with tin, silver, and gold, however, the influence of platinum becomes apparent. With the proper proportion of mercury, it seems to confer upon such an alloy the property of almost instantly setting, as well as much greater hardness. Thus, it will be seen that the qualities claimed for platinum *per se* belong in reality to the combination of tin, silver, gold, and platinum with mercury, since if either one of the others is omitted the platinum does not even remain passive, but actually by its presence causes marked deterioration of the qualities essential in a dental amalgam.

Alloys containing platinum amalgamate less readily than those wherefrom it is absent ; yet when union has once begun they seem to require a larger quantity of mercury to render them plastic. By careful experiment, the author found that with an alloy of

Platinum	500 milligrammes,
Gold	500 “
Silver	2000 “
Tin	2500 “

the smallest amount of mercury which could be employed without impairing the strength and general working qualities of the amalgam, was 300 milligrammes to 500 milligrammes of the alloy ; while with another ingot composed of

Gold .	500 milligrammes,
Silver	2000     “
Tin	2500     “

160 milligrammes of mercury to 500 of the alloy afforded a perfectly good result.

The proper quantity of mercury should be ascertained by careful experiment, as the statements of manufacturers or venders are not always reliable.

In order to ascertain the proportion of mercury required by different alloys, a small quantity of the latter should be taken, say one gramme, and, after weighing, the mercury may be carefully added and mixed by rubbing until the mass assumes a semi-coherent state. It should then be weighed again, to determine accurately how much mercury is present. It may then be introduced into a glass tube and condensed by means of instruments slightly warmed. Should the proportions not be correct, another trial may be made, and the quantity of mercury increased or diminished as indicated by the results of the first experiment.

The quantity of mercury required by each alloy is probably definite, so that a tolerably accurate approximation of the composition of an alloy should be ascertained by carefully noting the required proportions of one to the other.

Different methods are employed for the attainment of this object. Probably the most common is to mix the alloy with a large excess of mercury, and then to express the surplus of mercury either by compression with the fingers or through the pores of a piece of chamois-leather. The first involves the loss of some of the alloy, which is carried away with the surplus

of mercury, and neither is to be relied upon as a means of excluding an excess of mercury.

There are also several methods employed in mixing amalgams. Probably the most common one consists in simply rubbing the alloy and the mercury together in the palm of the hand. This is certainly the most expeditious, though not a very neat way, and much has been said about manifestations of the physiological effects of mercury following a long continuance of the practice. The author has made considerable effort to ascertain the correctness of this theory, in view of the fact that certain phases of ill-health have been attributed to absorption of mercury through this method of mixing amalgams, but he has been unable to trace a single case of ptyalism or any other well-marked sign of mercurial poisoning to this cause. It would be well to remember, however, that the active properties of mercury are developed by a state of fine division, and that there is nothing unreasonable in the theory that mercury, highly comminuted by rubbing in the palm of the hand, may find its way into the system and produce constitutional disturbance. In view of these facts, it would be a proper precaution to prevent contact of the mercury with the skin. This may be accomplished by covering the hand with a piece of rubber-dam, forming a sort of mitten, leaving the fingers free and having an opening for the thumb to pass through.

Small porcelain and glass mortars are also employed in promoting amalgamation, but they do not effect the desired purpose speedily, in consequence of the granules of the alloy becoming burnished by the

attrition of the pestle. Heating the mortar will, however, greatly facilitate union.

Mr. Fletcher has recently called attention to a simple and effective method of mixing amalgams. The required weight of filings and mercury are put into a long, narrow test-tube or bottle, and well shaken for a few seconds. The percussive force brought to bear upon the mass promotes prompt union.

Some difficulty may be encountered in introducing amalgam fillings when the mercury has been reduced to the minimum. The semi-coherent mass, almost in the form of a powder, is not easily conveyed to the cavity, especially if it is in the superior arch. Fletcher has devised a sort of mold by which amalgams mixed so dry as to be unmanageable ordinarily may be rapidly shaped into a convenient, workable form. It consists of a cylinder, into which the semi-coherent mass is poured. By means of a piston the powder is compressed into disks of the desired thickness, which may be introduced into the cavity and solidly compressed with slightly warmed instruments. It is claimed that this method practically does away with the chief objection to the use of very dry amalgams. Should the amalgam harden and become unmanageable before the completion of the filling, it may be rendered plastic and cohesive without disturbing the process of crystallization or the property of setting, by the use of slightly heated instruments. A further addition of mercury will be found to greatly impair, if not destroy, these properties.

Amalgams may be regarded as chemical compounds having definite proportions, and capable of being

dissolved in an excess of mercury, in which condition, however, they will no longer be found to fulfill the requirements of a filling-material. Hence, the operator should in no case attempt to restore the plasticity of an amalgam which has once hardened, by a further addition of mercury.

*Forming Alloys for Amalgams.*—The putting together of the constituents of an alloy composed of tin, silver, gold, and platinum, is a matter of no great difficulty, as it does not require an extraordinary degree of heat, and it may be easily accomplished in a stove or furnace such as is usually employed for heating or cooking purposes. The small reverberatory furnaces devised by Mr. Fletcher will be found to answer the purpose admirably. The author has used one successfully in a large number of melting operations. Their cost is only about \$3.50 each.

The only difficulty likely to be met in forming an alloy of this description is oxidation of the tin, and the formation of certain definite compounds having a tendency to separate from the mass, thus causing an ingot which is not homogeneous. Oxidation of the tin may take place at the instant of union with the platinum, and it is therefore preferable to melt the platinum and silver together first, and then add the tin and gold. A quantity of borax should be fused in the crucible before the metals are melted, the objects being to prevent adhesion of the alloy to the sides of the crucible, to facilitate pouring, and to dissolve and hold in solution any oxid which may be present. Lastly, a layer of broken charcoal should be placed over the mass before the heating. This will perfectly protect it from oxidation.

The formation of definite alloys, it has been shown, takes place with the gradual cooling of the mass ; the fusing-point and density of these being greater than of that which remains fluid, they manifest a tendency to settle to the bottom of the crucible in a solid state, and in some cases do not leave the crucible in pouring. Thus the ingot may not possess the desired composition. Again, the alloy may assume a semi-solid form, floating in masses in the more fluid portion, settling at the sides or bottom of the mold at the moment of pouring, the result being an ingot which is not uniform in composition, in consequence of which it has been recommended that different parts of every ingot should be tested ; but the difficulty may be entirely avoided by carrying the heat to the point of complete fusion and pouring while still very hot, before the tendency to separate is developed.

Oxidation of the surface from contact with the atmosphere will retard amalgamation. It is therefore better not to reduce the entire ingot to a state of fine division. It will be found to unite more readily with the mercury, if freshly filed off as required for use. This can easily be effected with one of the coarse files sold at the depots as vulcanite files.

Other metals, such as palladium, copper, cadmium, bismuth, antimony, and zinc, have been used as constituents of amalgams.

Copper is said to control shrinkage, while it increases the tendency to discoloration. It is also believed to exert a preservative influence on the tooth-structure. The salts of copper formed around amalgam fillings certainly do permeate and may protect the tooth-structure from further decay, but too much re-

liance should not be placed in the therapeutic theory in connection with this class of amalgams. It is exceedingly difficult to determine such a question. Amalgam is in many cases placed in teeth of such good quality that almost any filling-material would answer a conservative purpose, and the examples which are often presented of the long duration of such fillings may prove nothing beyond the density and superior quality of the tooth-structure. Careful and intelligent observation and experiment alone can satisfactorily solve a question of this kind.

Brittleness may be increased or diminished according to the quantity of platinum present, and the resulting amalgam will exhibit this quality equally with the alloy. An amalgam filling should always be strong enough to retain its integrity of edge under the force of mastication. A formula from which the author has obtained very good results is as follows :

Silver	40 grammes.
Tin	60 “
Gold	3 “
Platinum	3 “

Larger percentages of gold and platinum afford no better results,\* but, on the contrary, the alloy is rendered more brittle thereby ; its affinity for mercury is lessened, while its capacity for the latter is increased, as shown under the head of “Platinum.”

The more recent experiments with amalgams seem

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\*Under the assumption that amalgams are benefited in proportion to the amount of gold contained, Dr. W. G. A. Bonwill recommended that from 10 to 20 per cent. of gold be dissolved in the mercury used with the alloy. Dr. Bonwill has, however, ascertained by experiment that the above percentage was excessive, and when carried beyond a certain limit gold ceases to be useful to the amalgam.



to favor the substitution of zinc for platinum. The great improvement in amalgam filling-materials which was expected from the use of platinum has not been realized, but on the other hand alloys containing zinc instead of platinum have exhibited better qualities than had previously been attained. Soon after the publication of the first edition of this work, the author changed the above formula, using zinc instead of platinum, and the general working qualities of the amalgam seemed to be improved by the alteration. A number of fillings made with it at the time have since been frequently examined, and in maintenance of peripheral integrity and color have been in every respect satisfactory.

Since 1878 Dr. Louis Jack has conducted a series of careful experiments in the compounding of amalgams, in which he has kept accurate notes of the working qualities of each specimen and of the general results of each as developed by time. His first formula was :

No. 1.—Gold	$\frac{1}{2}$ oz.
Silver	2 “
Tin	3 “
Platinum	$\frac{1}{4}$ “

This was gradually modified in its proportions, until in 1885 the formula became :

No. 4.—Gold	$\frac{1}{2}$ oz.
Silver	$1\frac{3}{4}$ “
Tin	$3\frac{1}{4}$ “
Platinum	3 dwts.

The platinum still appeared to retard amalgamation, and cause blackening of the exposed surface of fillings. A new formula was adopted, from which

platinum was excluded, and pure zinc used in its place, as follows :

No. 5.—Gold	½ oz.
Silver	1¾ “
Tin	¾ “
Zinc	3 dwts.

Dr. Jack states that fillings of formula No. 5 have shown great durability, clearly maintained edge strength, and sufficient hardness to resist attrition on masticating surfaces, but they became so much discolored by the action of hydrogen sulfid that he gradually increased the quantity of gold, and slightly changed the ratio of the silver and tin, until formula No. 8 was reached :

No. 8.—Gold	14 dwts.
Silver	2 oz.
Tin	3 “
Zinc	3 dwts.

Fillings in the mouth composed of this alloy show but slight surface discoloration, and come very near to meeting all the requirements of a good filling-material if proper precautions in mixing are observed. To amalgamate readily, the alloy should be freshly filed, and with the minimum amount of mercury, which may be readily ascertained by experiment, union of the two may be obtained by violently shaking them in a test-tube, until the mass becomes somewhat plastic. It is then kneaded in a chamois-skin or napkin, this being done to prevent the oil and moisture of the hand from becoming incorporated with the amalgam, which Dr. Jack considers of great importance. The consistence of the mass should be such that it is inclined to be friable. The material is then

cut into pieces and packed, piece by piece, either with the automatic mallet with broad, flat points, or with heated pluggers. Should free mercury appear on the surface, this should be scraped away, and the filling completed with dry pellets.

Dr. Jack states that it is doubtful what part the zinc plays as an ingredient of amalgams, but he is now engaged in a series of experiments to determine its true value by omitting it entirely from formula No. 5 and carefully noting the effect.

It is of importance that all the different metals taking part in the formation of amalgam alloys should be pure, and in mixing the alloy for introduction into the cavity the utmost dryness and cleanliness be maintained; and of course it is understood that no test-filling of amalgam can be fairly made unless the thorough preparation of the cavity and all other conditions of successful filling have been carefully performed.

Among the important facts elicited by Dr. Jack's investigations are that platinum as a constituent in amalgam alloys is of questionable use, and that a larger proportion of gold than is given in formula No. 8 is impracticable, since an increase beyond that amount prevents setting, and the mass remains too soft for a filling-material.

The following are the different formulas employed by Dr. Jack in his investigations since 1878 :

No. 1.		No. 3.	
Gold	$\frac{1}{2}$ oz.	Gold	$\frac{1}{2}$ oz.
Silver	2 "	Silver	2 "
Tin .	3 "	Tin	3 "
Platinum	$\frac{1}{4}$ "	Platinum	$3\frac{1}{4}$ dwts.

No. 4.	
Gold	$\frac{1}{2}$ oz.
Silver	$1\frac{3}{4}$ "
Tin	$3\frac{1}{4}$ "
Platinum	3 dwts.

No. 5.	
Gold	$\frac{1}{2}$ oz.
Silver	$1\frac{3}{4}$ "
Tin	$3\frac{1}{4}$ "
Pure Zinc	3 dwts.

Has always shown good results, but exhibits surface discoloration.

No. 6.	
Gold	$\frac{1}{2}$ oz.
Silver	$1\frac{1}{2}$ "
Tin	$3\frac{1}{2}$ "
Pure Zinc	4 dwts.

No. 7.	
Gold .	12 dwts.
Silver	$1\frac{3}{4}$ oz.
Tin	$3\frac{1}{4}$ "
Pure Zinc	8 dwts.

No. 8.	
Gold	14 dwts.
Silver	2 oz.
Tin .	3 "
Pure Zinc .	3 dwts.

Results uniformly good.

No. 9.	
Gold .	14 dwts.
Silver	$2\frac{1}{4}$ oz.
Tin	$2\frac{3}{4}$ "
Pure Zinc .	3 dwts.

No. 10.	
Gold	16 dwts.
Silver	2 oz.
Tin	3 "
Pure Zinc	3 dwts.

Too soft, and suffered some loss by surface waste.

No. 11.	
Gold	$\frac{1}{2}$ oz.
Silver	$1\frac{3}{4}$ "
Tin	$3\frac{1}{4}$ "

From actual experience with Nos. 5 and 8, the author can testify to the excellence of their general working qualities and their durability. They afford, however, very quick amalgams, and should not be mixed with mercury until the cavity is quite ready for the reception of the filling ; or, if found to set too quickly, that quality may be modified by using less gold in the formula.

Palladium and mercury are said to make a very good filling. According to Mr. Thomas Fletcher, however, all alloys into which palladium enters as a constituent are utterly worthless; combined with tin and silver, it has been found to be unsatisfactory. Mr. Fletcher gives the results of a number of experiments with tin, silver, and palladium.\* "The alloys given below were made from chemically pure metals. They were melted first at a high temperature, under a layer of charcoal, in a clay crucible, with constant stirring. They were then poured quickly into a thick and cold iron ingot-mold; broken up and remelted three times, to insure uniformity as far as possible.

Pd. 1, Ag. 5. Result powdery and unmanageable.

Pd. 1, Ag. 5, Sn. 1. Result ditto. Both readily combined with Hg.

Pd. 1, Ag. 5, Sn. 2. Result same as above.

Pd. 1, Ag. 5, Sn. 3. Result very dirty to mix; makes a leaky plug.

Pd. 1, Ag. 5, Sn. 6. Result similar to last.

Pd. 1, Ag. 3, Sn. 5. Result very dirty; does not combine properly with mercury.

Pd. 1, Ag. 6, Sn. 5, Au. 1. Result similar to last.

Pd. 1, Sn. 4. Result very dirty; does not set at all."

In consequence of the uniformly bad results of these combinations, Mr. Fletcher discontinued further experimentation in palladium alloys for dental amalgams.

The claim, however, has been made for palladium, †

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\*British Journal of Dental Science.

†Dr. Bogue, in Proceedings of New York Odontological Society, Dental Cosmos, 1884, p. 403.

that when used as a single metal amalgamated with mercury, like Sullivan's amalgam (copper and mercury, see chapter on "Copper"), it does not change in form or bulk, or discolor the teeth, and though it turns quite black, it is a thoroughly reliable filling provided the cavity be properly prepared. It is said that the union of palladium and mercury is a true chemical one, and is accompanied with the phenomena usual in such cases of heat and incandescence.

*Qualitative and Quantitative Examinations of Amalgam Alloys.*—It is important for the dentist employing filling-materials of this class to be well informed as to their composition, and it is also often desirable to be able to determine the composition of old amalgam fillings, the constituents of which, besides tin and silver, are unknown.

With a compound belonging to the latter class the first step, after weighing, would be to free it from mercury by heating to redness, the loss of weight at the second weighing indicating the amount of mercury which was present. After this it is to be treated as an alloy, one gramme of which may be placed in a test-tube or other suitable glass vessel, and acted upon by a sufficient quantity of chemically pure nitric acid. The silver is dissolved and converted into argentic nitrate. The tin is oxidized and becomes metastannic acid ( $5\text{SnO}_2, 10\text{H}_2\text{O}$ ). The latter, in the form of a white powder, settles to the bottom of the vessel. If gold forms part of the alloy, it will be recognized, even in the smallest quantity, by the very decided purple color which it imparts to the precipitate, due to the formation of purple of Cassius. Platinum may be

readily detected by the presence in the test-tube of the finely divided metal, quite black in color.

At this point in the experiment, if neither gold nor platinum is present, the quantitative estimation of the alloy is not difficult, and may be accomplished as follows: The solution should be rendered neutral by evaporation, and diluted with a large quantity of distilled water. The oxidized tin will be found at the bottom of the vessel. After pouring off the solution, this should be washed, dried, and rendered anhydrous by heating to redness, when it is ready for weighing, every 100 parts indicating 78.66 of tin. Returning to the solution, the silver is next precipitated by sodium chlorid or hydrochloric acid, and may be collected by filtering.

If cadmium is present in the remaining solution, sulfuretted hydrogen will throw it down in the form of a yellow powder (sulfid of cadmium), the color distinguishing it from zinc sulfid, which is white. The alkalies, potassa, soda, and ammonia throw down the oxid of cadmium as a white hydrate. Ammonic carbonate also produces a white precipitate, which is insoluble in excess of the precipitant. The latter quality also distinguishes it from zinc, which is soluble under similar conditions.

Zinc may be precipitated from a solution by potassic carbonate, added in sufficient quantity to decompose any ammoniacal salts, if present, as such would prevent the precipitation of the carbonate of zinc. The whole is now to be evaporated to dryness, hot water added, the zinc salt boiled, collected by filtering, and lastly, after washing, ignited to drive off the carbonic acid, when oxid of zinc remains. In quan-

titative estimation, zinc is always weighed in this form, the oxid being calculated as containing 80.24 per cent. of the metal.

If copper be present, as it frequently is in amalgam alloys, it will be instantly detected by the greenish hue which it imparts to the solution, after the "breaking-up" by nitric acid. Indeed, the appearance of the contents of the test-tube will, after the student has acquired some experience, serve to convey a pretty clear idea of the composition of the alloy. For instance, take one gramme of Arrington's alloy, composed of pure tin and silver, and act upon it with nitric acid; the contents of the test-tube will be a colorless liquid and a perfectly white powder. In another test-tube dissolve some of Lawrence's alloy, and the nitrate, instead of being perfectly colorless as in the preceding experiment, will show a decidedly green tinge, and the presence of copper is verified by the blue color developed by the addition of ammonia. Gold and platinum will be detected in alloys containing these metals by the appearances already described.

The presence of copper having been verified, that metal may be precipitated as cupric sulfid, by sulfuretted hydrogen. It may then be collected by filtering, and after washing and drying may be oxidized by nitric acid, and again be precipitated by potassa, and may then be weighed as an oxid. Should copper and cadmium both be present, the precipitate obtained by sulfuretted hydrogen will consist of sulfids of cadmium and copper. Boiling in dilute sulfuric acid, however, dissolves the cadmium so that the copper may be collected by filtering,



after which the cadmium may be again thrown down by sulfuretted hydrogen.

The merest trace of copper in solution may also be detected by placing a drop of the latter on a strip of clean platinum foil and touching it with a point of zinc. A spot of reduced copper will instantly appear.

For the quantitative analysis of an alloy containing tin, silver, gold, and platinum, the first step should be to remove the tin by deflagration. This is accomplished by placing the alloy, after weighing, in a small crucible with some borax, and heating to bright redness. While at that high temperature small portions of potassium nitrate are added. This is decomposed; its oxygen unites with the tin, converting it into stannic oxid ( $\text{SnO}_2$ ). After cooling, the crucible may be broken, and the remaining button, together with any small globules which may adhere to the sides of the crucible, collected and weighed, the loss indicating the amount of tin which was present. If the deflagration has been thoroughly performed, the button will be entirely freed of tin, and it then remains to separate the silver from the gold and platinum. This may be accomplished either by nitric or sulfuric acid. But, as the former will dissolve a considerable portion of the platinum along with the silver, sulfuric acid, which does not thus affect the platinum, affords more accurate results, and is the agent usually employed in parting operations where the alloy consists largely of silver, with an appreciable percentage of platinum.

The button, now consisting of silver, gold, and platinum, should be rolled into a thin ribbon, and

then placed in a glass or platinum vessel with at least two and a half times its weight of concentrated sulfuric acid. This is boiled, during which strong action is evinced by copious disengagement of sulfurous anhydrid, and the silver is converted into a sulfate. The boiling is continued until all the silver is dissolved, when the gold and platinum will be found at the bottom of the digester. The liquid is now poured off, and the silver recovered from the sulfate solution by precipitation with plates of copper, which reduce it in a more or less crystalline state. The remaining alloy, now consisting of gold and platinum, should be thoroughly washed, dissolved in nitro-hydrochloric acid, neutralized by evaporation, then dissolved in a large quantity of distilled water. It is then ready for precipitation with oxalic acid, by which the gold is thrown down, and the platinum remains in solution for subsequent treatment. The gold, which is now easily collected, should be washed, dried, and heated to redness, when it is ready for weighing.

Lastly, the platinum may be recovered from the solution by precipitation with ammoniac chlorid. When washed and dried it will be ready for weighing, and every 100 parts may be considered as containing 44.28 of platinum.

The composition of some of the principal dental amalgam alloys now in use, is shown in the following tables :

COMPOSITION OF SOME OF THE WELL-KNOWN DENTAL ALLOYS.\*

	Tin.	Silver	Gold.	Plat- inum.	Copper.	Zinc.	Cad- mium.	Anti- mony.	Pal- ladium.
Arrington's (S. S. White's).....	57.5	42.5							
Blackwood's G. and P. Alloy.....	56.85	42.00	0.50	0.15		0.50			
Best (Spencer & Crocker's) Old.....	61.5	34.5	5	0.5	3.5				
Chicago Renning Co.'s (Old).....	56.00	37.00		2.00					
Chicago Renning Co.'s (New).....	58.37	37.55	4.00	0.10					
Chase's Coppered Amalgam.....	50.	50.			10.			5.	
Chase's Plastic Tin Amalgam.....	50.	50.						7.	
Chase's Alcohol Tight Amalgam.....	40.	50.						10.	
Chase's Stannous Gold.....	40.	40.	20.						
Chase's Incisor Tooth Amalgam.....	40.	50.						10.	
Caulk's White Alloy.....	35.00	43.65			1.35				
Caulk's Par-Excellence.....	61.75	27.25	0.15	0.25	10.60				
Crown Gold Alloy.....	52.85	47.00	0.15						
Dawson's White Alloy.....	49.27	48.24	0.05			2.44			Trace.
Dawson's Superior Amalgam.....	63.55	31.85	0.65	0.15	2.35	1.45			
Dibble's White Amalgam.....	49.65	49.75	0.20			0.40			
Fry's Amalgam.....	53.80	44.35		0.90		1.05			
Fletcher's Gold Alloy (Old).....	50.	40.	4.						
Fletcher's Platinum and Gold Alloy.....	50.35	43.35	3.35	1.30	1.65				
Flagg's Submarine.....	35.	60.			5.				
Flagg's Facing.....	35.	37.	5.			3.			
Flagg's Contour Alloy.....	37.	58.	5.						
Globe (S. S. White's).....	53.36	44.74	1.50	0.40					
Grimes's Front Tooth (Old).....	44.	10.					46.		
Hood's Amalgam (Old).....	60.25	37.	2.75						
Hood & Reynolds's Gold and Platinum Alloy.....	50.40	44.30	3.80	0.30		1.20			
Hood & Reynolds's Sans Tache Alloy.....	50.00	47.90			0.30	1.80			
Holmes's Star No. 1 (Old).....	59.	46.	1.						
Holmes's Star No. 2 (Old).....	58.	39.5	2.	0.5					
Hays's Pure White (Old).....	51.5	43.5		1.					
Hardman's Amalgam.....	44.57	50.12			5.31				
Hardman's White Alloy.....	50.56	44.57	0.28		4.59				

\* American System of Dentistry.

COMPOSITION OF SOME OF THE WELL-KNOWN DENTAL ALLOYS.\*—Continued.

	Tin.	Silver.	Gold.	Plat- inum.	Copper.	Zinc.	Cad- mium.	Anti- mony.	Pal- ladium.
High Grade (7½ per cent. Gold).....	41.5	49.	7.5	.....	.....	2.	.....	.....	.....
Harris's (Prof. J. H.) Amalgam.....	48.10	40.00	.....	.....	4.90	7.00	.....	.....	.....
Johnson & Lund's Extra (Old).....	60.	38.00	1.5	0.5	.....	.....	1.45	.....	.....
Johnson & Lund's Extra (New).....	61.15	36.75	0.15	0.50	.....	.....	.....	.....	.....
Johnson & Lund's Virgin White Alloy.....	61.65	37.75	.....	.....	.....	0.60	.....	.....	.....
Johnson & Lund's Atlas Amalgam.....	61.90	36.85	.....	.....	.....	.....	0.90	.....	.....
Johnson & Lund's Extra Tough Alloy.....	51.25	47.00	0.30	0.35	0.25	.....	.....	.....	.....
Justi's Superior Gold and Platinum Alloy.....	59.10	35.20	0.32	0.08	3.50	1.80	.....	.....	.....
King's Occidental.....	54.75	42.75	.....	.....	.....	2.50	.....	.....	.....
Lawrence's (Old).....	47.	47.	1.	.....	5.	.....	.....	.....	.....
Lawrence's (New).....	50.43	44.06	.....	.....	5.51	.....	.....	.....	.....
Moffitt's (Old).....	62	36	2.	.....	.....	.....	.....	.....	.....
(Moffitt's) The Dentist's Amalgam.....	59.50	37.90	.....	.....	.....	2.60	.....	.....	.....
Oliver's Amalgam (Old).....	56.8	46.1	1.7	1.4	.....	.....	.....	.....	.....
Oliver's White Amalgam (New).....	55.25	44.74	.....	.....	.....	.....	.....	.....	.....
Peirce's (Old).....	40.	55.	4.	.....	.....	1.	.....	.....	.....
Prof. Essig's (Old).....	55.	45.	2.5	2.5	.....	.....	.....	.....	.....
Parsons's Eureka Silver Alloy.....	40.00	55.00	.....	.....	3.00	2.00	.....	.....	.....
Sterling Amalgam (Old).....	62.00	31.	1.	.....	6.	.....	.....	.....	.....
Sterling Amalgam, D. & L. (New).....	62.37	33.20	.....	0.14	4.33	.....	.....	.....	.....
Standard Amalgam (Davis & Co.).....	55.40	44.60	.....	.....	.....	.....	.....	.....	.....
Standard Dental Alloy (Eckfeldt).....	40.60	52.00	4.40	.....	3.	.....	.....	.....	.....
Shattuck's Standard Gold Alloy.....	51.74	46.98	1.20	0.08	.....	.....	.....	.....	.....
Sibley's Gold and Platinum Alloy.....	54.65	43.15	0.20	2.00	.....	.....	.....	.....	.....
Temporary Alloy.....	88.	10	.....	.....	.....	.....	.....	.....	.....
Townsend's (Old).....	58.	42.	.....	.....	.....	2.	.....	.....	.....
Townsend's (Improved).....	54.50	44.50	1.	.....	.....	.....	.....	.....	.....
Walker's (Old).....	60.	30.5	.....	.....	.....	.....	.....	.....	.....
Walker's Excelsior Gold and Platinum Alloy.....	51.50	42.00	0.30	0.5	6.00	.....	.....	.....	.....
Weich's Gold and Platinum Alloy (Old).....	54.	44.	1.3	0.7	.....	.....	.....	.....	.....
Weich's Gold and Platinum Alloy (New).....	51.90	46.00	1.70	0.40	.....	.....	.....	.....	.....
Weich's Amalgam.....	51.52	48.48	.....	.....	.....	.....	.....	.....	.....

\* American System of Dentistry.

The following formula, with directions for forming the alloy, kindly furnished by the late Dr. Ambler Tees, was highly recommended by that gentleman as affording excellent results :

Tin	40 dwts.
Silver	24 “
Gold	1 dwt.
Platinum	1 “

“ The gold, silver, and platinum to be melted first with borax and kept in a state of fusion for five minutes. The tin to be melted in a separate crucible, and the molten silver, gold, and platinum to be poured into the fused tin, and the whole quickly poured into a suitable ingot-mold and reduced to powder with a large machinist's file.”

## CHAPTER VI.

### MODES OF MELTING METALS.

VARIOUS forms of heating apparatuses, furnaces, etc., are of great importance to those who conduct metallurgical operations on a large scale. We shall, however, in these pages confine ourselves exclusively to the needs of the dental laboratory,\* including a consideration of the appliances for soldering.

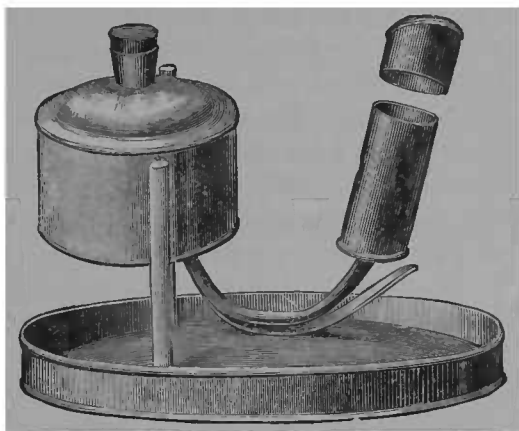
These operations are performed by the use of the oil or alcohol-lamp, or the gas-jet, or by means of a suitable stove or furnace. When kerosene oil or alcohol is employed, it is of the first importance to select a lamp designed not only to meet the practical requirements, but also with a view to safety. The first essential is to have the wick large enough to afford a flame of sufficient magnitude to enable the operator to solder an entire artificial denture, or to fuse from one to two ounces of gold. This would require a wick one and a quarter inches in diameter, and about three inches long. Its connections with the reservoir or body of the lamp in which the combustible fluid is contained should not be direct nor in such close proximity that explosive gas would

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\*Full and detailed descriptions of the different heating apparatuses, together with the most approved processes of reducing ores and of melting large quantities of metals, will be found in Percey's, Phillips's, and Makins's works on metallurgy.

be likely to form. The Franklin Safety Lamp, a cut of which is annexed (Fig. 1), will be found to answer every requirement. It consists of a reservoir five inches in diameter by two and a half inches deep. The wick-holder, three inches long by two and a half inches in diameter, is connected with the reservoir by a curved tube five inches long by three-sixteenths of an inch in diameter. Thus a sufficient quantity of the burning-fluid is supplied to the wick to afford

FIG. 1.



a constant flame, while there is no danger of the heat from the wick-holder being conducted to the reservoir to cause an explosion.

In cities and large towns where gas is available, that agent is to be preferred, on account of its greater safety and convenience. A gas-burner which will be found to answer every requirement of the laboratory may be constructed by attaching to the base of an ordinary Bunsen burner, such as is sold at the dental depots, a piece of brass tubing six inches in length

by one and a quarter inches in diameter. Over the top of this, in order to properly spread the flame, a piece of fine brass wire-gauze is fastened by means of a ring of sheet-brass, one-quarter of an inch in width. Connection may be obtained with the gas-bracket in almost any part of the room by means of flexible rubber tubing. This will be found to answer all purposes of soldering as well as of melting small quantities of gold and silver.

The blast and the flame are produced by the blow-pipe,\* an instrument which has long been used by workers in metals for the purpose of soldering together small pieces of metal, and for melting and reducing purposes generally. The ordinary form consists of a conical brass tube, from two hundred to two hundred and thirty or forty millimeters long, curved at the narrower end to nearly a right angle, so that the flame may be conveniently directed upon the piece of metal to be soldered or melted, as the case may be, which is held upon some suitable support, such as a piece of charcoal, coke, or pumice-stone. When the blow-pipe is used in its simplest form, by the mouth, the large end of the instrument is held between the lips, and the small end toward the flame. The blast should not be sustained by the respiratory organs, but, in order that an unbroken current may be kept up, the mouth should be filled with air, to be forced

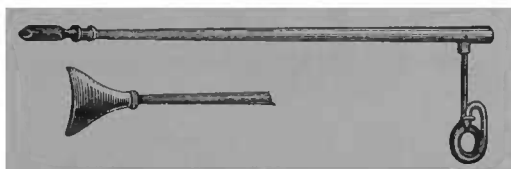
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\*The use of the blow-pipe for analytical purposes is credited to Anton von Swab, a Swedish Councillor of Mines, who made use of the instrument in the discharge of his official duties as early as 1738. Since that date its use has been widely extended, and the importance of reactions in the dry way produced under the flame of the blow-pipe is fully recognized and established. For full information on the subject the student is referred to Plattner's "Manual of Blow-pipe Analysis."



through the blow-pipe by the muscles of the cheeks. While these are forcing the air through the blow-pipe, the connection between the chest and the cavity of the mouth should be closed by the palate, which thus performs the part of a valve. The beginner is liable to fall into the error of not closing the connection between the chest and the mouth at the proper instant, and of obtaining the force necessary to propel the air through the blow-pipe from the lungs. That this manner of using the instrument may injure the organs of respiration cannot for a moment be doubted, and the operator should early acquire the proper method, above described. To avoid tiring the muscles of the lip by continual blowing, the trumpet

FIG. 2.



mouth-piece has been recommended and is shown in the annexed cut, Fig. 2. This is merely pressed against the open mouth, and an uninterrupted blast may be kept up for a long time without causing the least fatigue of the orbicularis oris, since that muscle takes but a passive part in the operation. This trumpet-piece, however, should be so curved as to correspond with the shape of the mouth, otherwise it will require to be pressed very forcibly against the lips in order to prevent the escape of air.

The blow-pipe should be constructed of either brass or German silver, as these alloys are but poor

conductors of heat. Silver is not well suited for the purpose, because it transmits temperatures so readily that it soon becomes too hot for the fingers.

A long-continued and steady flame maintained by the mouth blow-pipe is apt to cause disturbances in the flame from the collection of moisture in the tube, which is liable to be expelled by the pressure of the air. To avoid this a hollow chamber is constructed about midway in the instrument. The length of the instrument should be adapted to the eye of the operator, so that the object upon which the flame is directed may be distinctly seen.

An improvement in these instruments has been made by Mr. Thomas Fletcher, F.C.S., of Warrington, England (see Fig. 3), by which temperatures

FIG. 3.

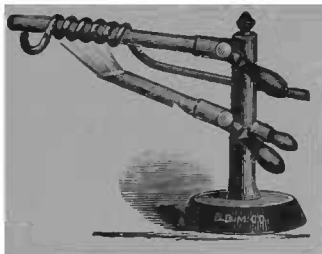


beyond those which can be produced by the ordinary gas and air blow-pipes are attainable. It not only gives temperatures never approached with the old blow-pipe, but it is also in every respect more convenient, easier to use, and better adapted for every class of work. With the same amount of blowing as with the common form, this blow-pipe will do nearly double the work; if high temperatures are not required, the labor of blowing is reduced in proportion. The improvement consists in coiling the air-tube into a light spiral *over the point of the jet*. This coil takes up the heat which would otherwise be wasted, and utilizes it by heating the air in its passage. The author has found this form of mouth blow-pipe to be

well adapted for fine analytical operations by cupellation, as well as for all uses of the dental laboratory.

Fletcher's hot-blast blow-pipe is so constructed that the air-pipe is coiled around the gas-pipe in a spiral form, and both are heated by three small Bunsen burners underneath, which are controlled by a separate stop-cock, as shown in Fig. 4. It is claimed that the power of this apparatus is about double that of an ordinary blow-pipe; that when the jet is turned down to a small point it will readily fuse

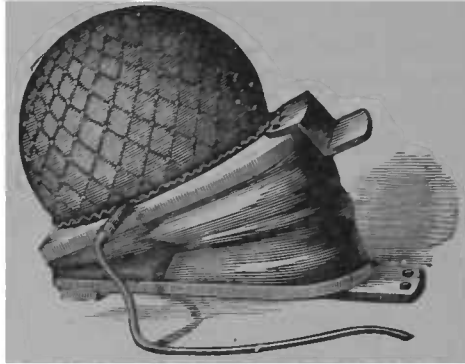
FIG. 4.



a moderately thick platinum wire, and that its power is nearly equal to the oxyhydrogen jet. This form of blow-pipe is well adapted to continuous-gum work where the teeth are soldered to the plate with pure gold. The blast is obtained by means of a foot-blower (Fig. 5), connected with the blow-pipe (Fig. 4) by a flexible rubber tube. The reservoir of the upper portion, which holds the air, is, when the bellows is not in operation, merely a disk of thick coffer-dam rubber, which expands under the pressure of the air while the bellows is in motion, and thus affords a very compact, powerful, and effective arrangement. The step for the foot is very low and the blower may be used with

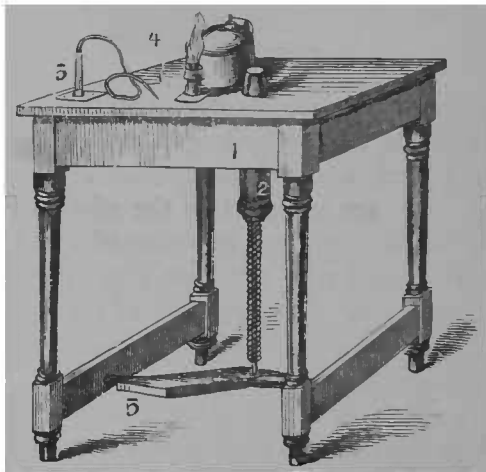
ease, whether the operator is standing or seated. The pressure is perfectly steady and equal. If the rubber

FIG. 5.



disk is distended until forced against the net, the pressure can be increased to almost any extent desired.

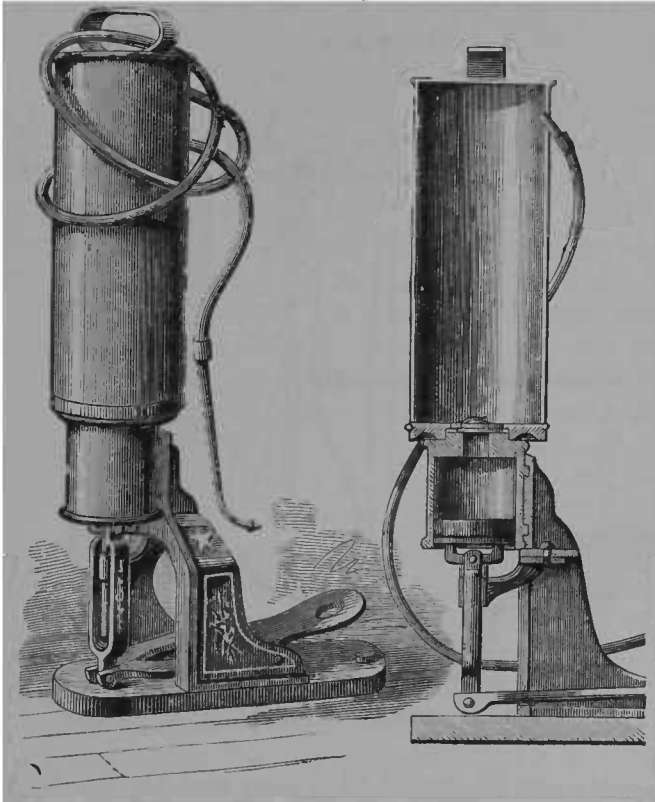
FIG. 6.



It will give, if required, a heavy and continuous blast through a pipe of a quarter-inch clear bore.

The mechanical blow-pipe is not a new idea. It has been in use by dentists for nearly fifty years, and in extensive soldering operations is one of the most

FIG. 7.



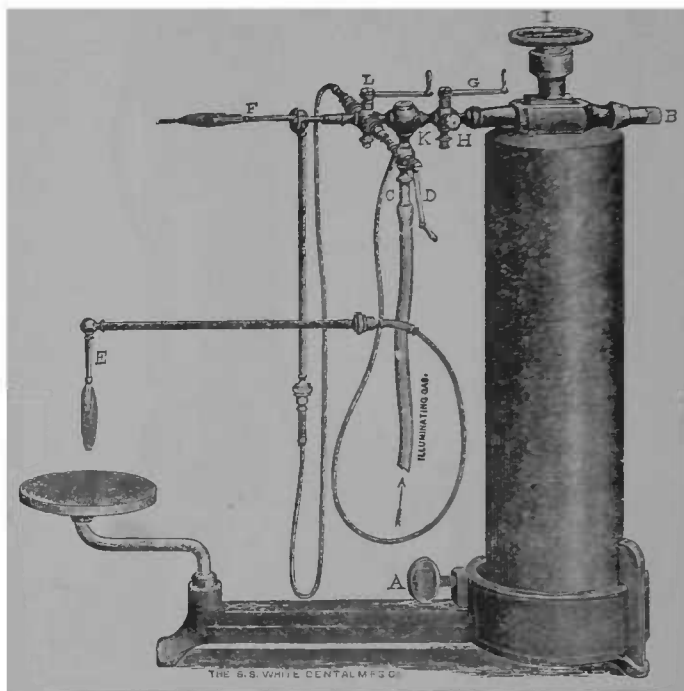
valuable appliances of the dental laboratory. The instrument as formerly made by the late Mr. Bishop, of Philadelphia, is probably superior to the more recent forms (see Fig. 6).

The Burgess blow-pipe, illustrated in Fig. 7, is con-

structed on exactly the same principle as the above, and is convenient and effective.

The form of oxyhydrogen blow-pipe invented by Dr. J. Rollo Knapp, is perhaps the most complete and effective apparatus for soldering and melting

FIG. 8.



operations in the dental laboratory that has yet been devised. It may be used with equal facility in soldering the largest piece of plate-work, or the most delicate crown-work, and is of particular value to dentists who give attention to continuous-gum work, enabling them to readily remelt their platinum scraps.

It is provided with an iron stand in which is secured by a thumb-screw a 100-gallon cylinder of nitrous oxid gas. By means of a yoke and set-screw, the valve of the cylinder is connected with the tubes and valves of the blow-pipe in such manner that the proportions of a mixture of nitrous oxid and illuminating gases are under perfect regulation and control.

A cylinder of nitrous oxid gas is placed in the base or stand, and fastened with the thumb-screw A. The yoke carrying the stop-cocks and valves is attached to the valve of the cylinder, and tightened with the screw B. The pipe C is connected by a rubber tube to an illuminating-gas bracket. When the apparatus is in use the illuminating-gas is turned on, and its flow regulated by the handle D. The handle G, over the outlet H, is then turned, the cylinder valve is opened by means of the hand-wheel I sufficient to permit the escape of enough nitrous oxid gas to be detected by touching the opening H with the finger.

When the desired quantity of nitrous oxid gas is obtained, the flow is directed to the mixing chamber and controlled by the handle G, which, when in position, as shown in the cut, allows the gas to pass freely into the chamber K, where it mixes with the illuminating-gas.

Either or both of the burners may be used, and the desired flame obtained by regulating the pressure of the gases by the handles controlling them. It is an instrument of much greater delicacy than the blow-pipes commonly used by dentists. The flame which it affords is very small, but the intensity of its heat is such that great care must be exercised in soldering small objects to prevent burning or even

entire fusion of the parts adjacent to the solder. It is economical of time and materials, and its perfect cleanliness will commend it to all who work in the higher branches of mechanical dentistry.

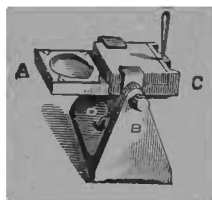
When a small quantity of gold or silver is to be melted by means of the blow-pipe, it is usually performed upon a support formed of charcoal. A good solid cylindrical piece of thoroughly charred pine coal should be selected, and divided into two equal halves by a vertical cut with a saw. Upon the end of one half a depression should be cut for the reception of the metal to be melted. On the flat side of the other half, extending to the end, the ingot-mold should be carved, of size and shape governed by the requirements of the case. The two halves should then be brought together and secured by a piece of iron or copper wire, when they will be found to practically combine the requirements of crucible and ingot-mold. The depression in which the metal is to be melted and the mold or receptacle should be connected by means of a gutter or groove. The flame is now directed upon the metal, and when thoroughly fluid the charcoal is tilted so that the fused metal will run into the mold prepared for it in the opposite half of the charcoal. This is probably the simplest form of apparatus by which small quantities of metal can be melted, and is often employed in the dental laboratory and by jewelers.

Fletcher has devised an apparatus embodying the same general principles as the one just described, for quickly obtaining ingots of gold and silver without the use of a furnace. It is shown in the accompanying diagram (Fig. 9); A, representing a crucible of



molded carbon, supported in position by an iron side-plate ; C, the ingot-mold ; D, clamp, holding ingot-mold and crucible in position ; B, cast-iron stand upon which the latter swivels. The metal to be melted is placed in the crucible, A, and the flame of the blow-pipe directed upon it until it is perfectly fused. The waste heat serves to make the ingot-mold hot. The whole is tilted over by means of the upright handle at the back of the mold.

FIG. 9.



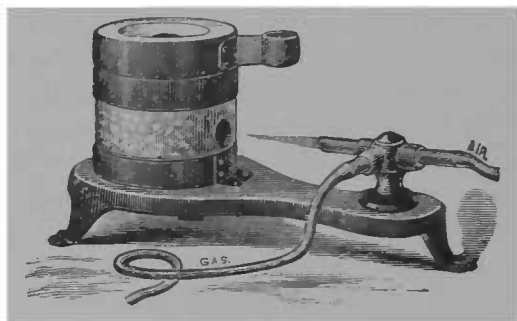
A sound ingot may be obtained by the use of this simple little apparatus in a very few minutes. Simple contrivances of this kind are, however, not applicable to melting operations involving quantities exceeding one ounce. In such cases it is better to employ a crucible and any stove or furnace in which the temperature can be raised sufficiently. This may be accomplished in an ordinary cooking-stove, a black-smith's forge, or a small fire-clay furnace, by the use of anthracite coal, coke, or charcoal.

By far the most convenient, compact, and effective furnace for melting from one to ten ounces of gold which has ever been used is the crucible-furnace (Fig. 10), invented by Mr. Fletcher, which can be obtained at the dental depots. The furnace is perfectly adapted to the wants of the mechanical dentist. It is composed of a substance resembling fire-clay, but much lighter in weight, and said to possess only one-tenth its conducting power for heat.

The furnace consists of a simple pot for holding the crucible, with a lid and a blow-pipe, all mounted on a suitable cast-iron base. As compared with the

ordinary gas-furnace it appears almost a toy, owing to its great simplicity. The casing holds the heat so perfectly that the most refractory substances can be fused with ease, using a common foot-blower. Half a pound of cast iron requires from seven to twelve minutes for perfect fusion, the time depending on the gas-supply and the pressure of air from the blower. The power which can be obtained is far beyond what is required for most purposes, and is limited only by the fusibility

FIG. 10.

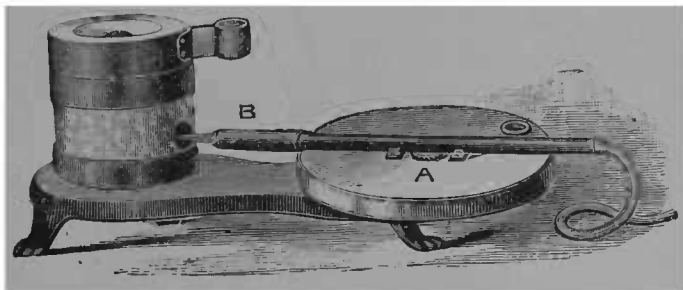


of the crucible and casing. The crucible will hold about ten ounces of gold. An ordinary gas supply-pipe of  $\frac{5}{16}$  or  $\frac{3}{8}$ -inch diameter will work it efficiently. It requires a much smaller supply of gas than any other furnace known; about ten cubic feet per hour is sufficient for most purposes. Crucibles must not exceed  $2\frac{1}{4}$  by 2 inches. Any common blow-pipe bellows will work the furnace satisfactorily, except for very high temperatures (fusion of steel, etc.), for which a very heavy pressure of air is necessary. In size it is but four inches in diameter by three in height. The author has used one in his laboratory for the

purpose of melting gold and silver and for general metallurgical experiments for several years, with the greatest satisfaction ; he has also found it to be most admirably adapted to class demonstration, for which purpose, as a means of illustrating his lectures on metallurgy, he has had frequent opportunities to use it.

A modification of the apparatus has been made, adapting it to the use of refined petroleum instead of gas as a fuel, and thus rendering it of more general utility (see Fig. 11). Thus improved, it is said to be

FIG. 11.



in no way inferior in efficiency to the gas-furnace. The burner of this furnace is constructed upon the principle of an atomizer, which, of course, dispenses with a wick ; it is supplied with a device for regulating the supply of oil, which is operated by the milled nut (marked A) shown on the top of the reservoir in the cut, and for the supply of an annular jet of air, which is regulated by turning the sleeve (marked B). This burner is so arranged that in case any obstruction should occur it can be taken apart and cleaned by separating the burner from the reservoir, which is accomplished by loosening the small screws,

drawing out the oil-tube, taking off the sleeve B, and removing the inside tube.

These furnaces are so constructed that they may be used for either gas or petroleum, the lamp being fitted for adjustment in place of the gas-burner, so that the same apparatus may be used for either. The blast is obtained by means of the foot-blower shown on page 80, which is connected with the furnace by means of India-rubber tubing, as seen in Fig. 11.

FIG. 12.



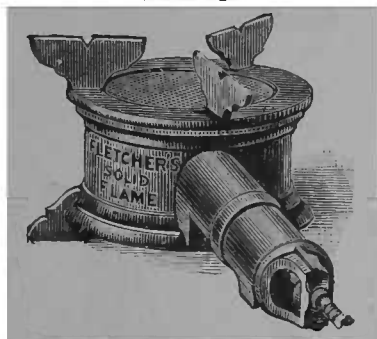
An injector gas-furnace has also been perfected by Mr. Fletcher, which seems to be well adapted to the wants of the dentist, chemist, or metallurgist (see Fig. 12).

The construction of this apparatus is upon the principle of the injector-furnace, and it is claimed that its power and speed of working are practically without limit, depending only upon the gas- and air-supply. With a half-inch gas-pipe and the small foot-blower (see page 80) this furnace will melt a crucible full of cast-iron scraps in ten minutes. The supply

of gas required is exceedingly small. Allowing five cubic feet of gas for heating up, it consumes about four feet of gas for every pound of cast iron melted. For laboratory purposes it is the cheapest and most convenient furnace in use. It is very simple in construction, and consists of two parts,—an upper portion, which forms the cover, and a lower part, which holds the crucible while in operation.

Mr. Fletcher has devised a gas-lamp which has given satisfactory results in melting zinc and lead for

FIG. 13.



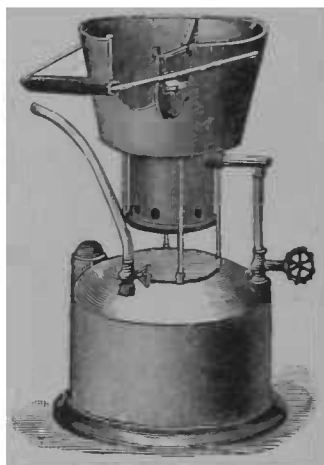
dies and counter-dies, and for the fusion of all alloys which may be accomplished in an iron ladle at or below a red heat (see Fig. 13).

When gas is not available the gasoline furnaces used by plumbers for melting solder have no superior in point of convenience and rapidity. These furnaces are made by C. Gefrörer, of Philadelphia, and are shown in Fig. 14.

*Crucibles.*—The term “crucible” is applied to a chemist’s melting-pot, made of earthenware or other material, and so called from the superstitious habit

of the alchemists of marking such vessels with the sign of the cross. The term is now generally understood as designating vessels in which metals are melted in furnaces at high temperatures. A crucible should possess the power of resisting high temperatures without fusing or softening. It should also be capable of retaining sufficient strength, when hot, to prevent its crumbling or breaking when grasped

FIG. 14.



by the tongs. Lastly, it should not crack either in heating or cooling.

For the purpose of melting metals crucibles are made of clay with admixture of silica, burnt clay, graphite, or other infusible material. For the fusing of platinum, which requires the intense heat of the oxyhydrogen flame, they are formed of lime. For use in the dental laboratory, graphite crucibles, which can be obtained at the dental depots, will be

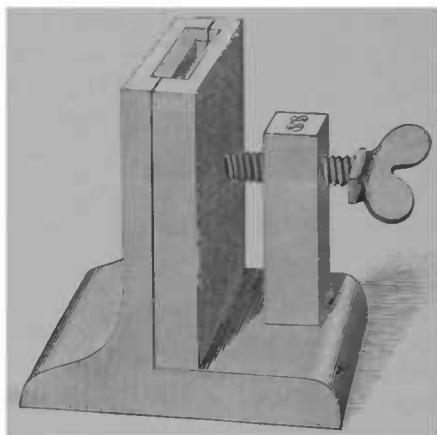
found to answer every purpose, and they are thoroughly reliable in strength and durability. They range in size from two to four inches high, and are specially adapted for use in the Fletcher gas-furnaces. When the quantity of metal to be melted is very small, say a half-ounce of gold, the smallest-sized Hessian crucible may be used in the small Fletcher apparatus.

Crucibles suitable for melting platinum or iridium are formed of two blocks of lime, each block having a concavity or excavation, so that when the two pieces are placed together the center is hollow ; it is thus designed to hold the scraps of platinum to be melted. The lower block is also arranged with a groove and lip, so that when the metal becomes fluid it may be poured into a suitable ingot-mold by inverting the crucible. The compound flame is introduced by tubes passing through the center of the upper block of lime forming the cover.

Before melting any considerable quantity of gold the crucible should be tested, particularly if the melting operation is to be performed in an ordinary coal-stove, where a defective crucible might be the means of a considerable loss. A small amount of borax should be placed in the vessel, which should then be exposed to a high temperature. Should it not be perfect, the borax glass will run through and glaze the surface on the outside. If the crucible is found to be impervious, it should be so inverted while yet hot that the borax glass may cover the surface of the lip or groove out of which the melted metal is to be poured. This facilitates the pouring and prevents any portion of the metal from adhering to the side of the crucible.

Ingot-molds are constructed of various substances. For the reception of platinum melted with the oxy-hydrogen blow-pipe they are formed of lime or coke; for gold and silver, they are commonly made of cast iron, about two inches square and from an eighth to three-sixteenths of an inch thick (see Fig. 15), with slightly concave inner surfaces, as the shrinkage of the ingot is greatest at the center. Ingot-molds

FIG. 15.



formed of soap-stone are also employed. The ingot-mold should be heated before pouring.

Rolling or laminating is accomplished by repeatedly passing the metallic ingot between cylindrical steel rollers from three to four inches in width. These are so arranged that, by means of screws, they are capable of being brought closer together every time the gold is passed through (see Fig. 16). The proper degree of attenuation is determined by the gauge-plate (Fig. 17). Gold or silver is made into



wire by means of the draw-plate,—an oblong piece of steel provided with a number of gradually diminishing holes enlarged on the side where the gold enters.

The gold to be drawn through may be prepared in a cylindrical shape by melting and pouring into an ingot-mold provided with a chamber for the purpose (some ingot-molds are so constructed). The end of the rod should be filed so as to readily enter the draw-plate, which must be firmly screwed in a vise.

FIG. 16.

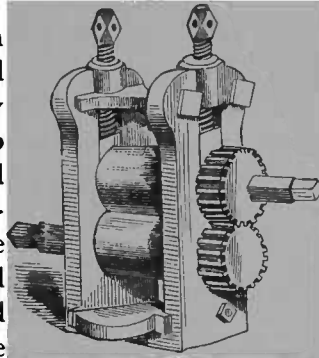
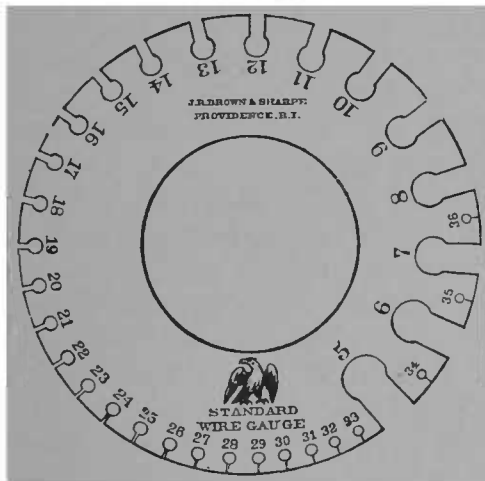


FIG. 17.



The gold is then, by means of a pair of strong pliers, drawn through the different holes of the draw-plate

consecutively until the desired size is reached. At the beginning of the operation it will require frequent annealing.

Soldering must also, to a certain extent, be regarded as coming under the general head of melting operations, since it refers to the union of two or more pieces of metal by means of a more fusible alloy. The conditions of successful soldering are : 1. Contact of the two pieces to be united. 2. A clean metallic surface over which the solder is to flow. 3. A freely flowing solder. 4. Proper amount and distribution of heat.

Contact of the pieces to be united is of the greatest importance. If, for example, the object to be soldered be an artificial denture, it is an indispensable requirement that the backings be quite or very nearly in contact with the plate, and, if gum teeth be used, that each backing touch its neighbor. This is not difficult to accomplish, if the teeth have been carefully and accurately fitted to the plate and to each other. If, however, any defects of this character are found to exist after the teeth have been invested, they should be remedied by filling such spaces or crevices with small pieces of gold or silver, as the case may be, thus rendering the continuity of the parts complete. By the observance of this precaution much of the vexation in soldering experienced by beginners may be avoided, and when the other conditions named have been observed the operation becomes exceedingly simple. Solder runs freely by the force of capillary attraction between two closely-fitting surfaces, just as water will be drawn against gravity between two panes of glass in close contact. In soldering artificial dentures which have been carefully arranged with refer-

ence to contact of all the parts to be united, the author has on several occasions completed the operation of soldering perfectly without using the blow-pipe at all, by merely heating the whole case to the fusing-point of the solder, in a charcoal furnace with a good draft. Thus it will be seen that the difficulties of soldering are mainly due to a violation of one or more of the rules herein given.

Cleanliness should always be strictly observed in soldering operations. The parts to be united should present bright and clean surfaces. Darkening or oxidation will always occur when gold or silver, the purity of which has been reduced by alloying, is heated to redness. A weak solution of sulfuric acid and water, slightly heated, will quickly remove discoloration resulting from this cause; or the borax employed as a flux in soldering operations will effect the same result, by dissolving\* the oxid which forms on the surface, while it also protects from further oxidation by excluding the oxygen of the atmosphere. The surfaces to be soldered should be carefully protected from any contact with plaster of Paris, as there is no substance used in the dental laboratory more likely to retard the union of the parts and impair the final result than this. To this end, all parts over which the solder is to flow should, previous to their investment in sand and plaster, be thoroughly covered with the cement of resin and beeswax commonly used in the dentist's laboratory as a temporary fastening for teeth, clasps, etc., which are to be united by soldering.

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\* Borax, when fused to a glass, has the quality of dissolving metallic oxids, and the different colors imparted to the "bead" is one means of discrimination in blow-pipe analysis.

This will effectually exclude plaster, and it is easily removed after the investment has sufficiently hardened.

A solder to be employed in dental mechanism should possess the quality of flowing freely, and be as high in grade as the attainment of that property will permit, so that it will sufficiently resist the action of the fluids of the mouth. It should also approximate as nearly as possible the color of the plate upon which it is used. If the first condition, referring to the contact of the plates to be united, be observed, the quantity of solder required to effect continuity may be reduced to the minimum; and thus we shall have the smallest possible portion of the alloy exposed to the action of the fluids of the mouth, while we at the same time avoid the danger of fracture of the teeth by the contraction in cooling of an inordinate quantity of solder. The latter, for all purposes of the dental laboratory, should be in the form of plate of say No. 27 in thickness, and this should be cut into portions of sizes corresponding to the extent of the parts to be united. Thus, upon each pin a small particle of solder should be placed, just large enough to cover it. A piece of the same size should also be placed near the top of each joint where the backings come together, while a larger piece should be placed at the points of union between backings and plate. These pieces of solder are made to adhere to their proper positions through the agency of the borax, which is used by taking a lump, rubbing it on a piece of ground glass with clean water to a creamy consistence, and then applying to the surface by means of a camel's-hair pencil.

The application and management of the heat in the

operation of soldering are matters requiring both care and judgment. The temperature should at first be raised very gradually, in order that pieces of solder may not be thrown off or displaced by the puffing-up incident to the calcination of the borax, or, in the case of an artificial denture, that the porcelain teeth may not be fractured by a too sudden elevation of temperature. Both parts to be united should be equally heated ; therefore the heat should be so applied in the case of an artificial denture as to raise the teeth and plate to an equal temperature ; otherwise, should the plate become sufficiently hot while the teeth remain comparatively cool (a condition likely to occur unless the fuel has been built up around the outside of the investment covering the teeth), the solder, when the flame of the blow-pipe is directed upon it, will flow upon and adhere to the plate. In other words, it will manifest a preference for the hottest portion. The failure to effect an equal distribution of heat preparatory to soldering is often the cause of much vexation and delay. For example, in the process of uniting a rim to a plate by soldering, the rim, being so much smaller than the plate, will be more quickly heated, in which event the solder will fuse and flow upon the rim, and the attempt to unite it to the plate will not be successful. But to avoid such a result the flame of the blow-pipe should, as a preliminary step, be directed exclusively upon the plate until it has been heated to nearly the fusing point of the solder, when the pointed blue flame may be directed upon the latter, and union of the rim and plate can hardly fail to take place.

*Supports.*—In melting small quantities of gold or silver, or in soldering with the blow-pipe flame, it is

necessary to perform these operations upon a support made of some suitable body, such as charcoal, coke, pumice-stone, or asbestos and plaster, charcoal and plaster, etc.

Well-burned charcoal is especially suited for both purposes, as it helps to increase the heat, and, in the putting together of small quantities of gold or silver solders, prevents oxidation of the base metals which are added to reduce the fusing-point of the alloy and cause it to flow freely. Charcoal made from the light woods, such as pine, is best, because it is not so likely to throw sparks when the flame is directed upon it as are the harder coals, such as that made from oak, and, being softer, it is much better adapted to soldering operations in which it is necessary to hold together the pieces to be united by means of small nails or tacks thrust into the support; as, for instance, where a rim is to be soldered to a plate, the former must be brought in contact with the latter upon the charcoal, and so held during the preliminary soldering, which consists of uniting the rim to the plate with a small piece of solder at some one point; after which the accurate adjustment of the rim to the plate for the final soldering is rendered much easier.

A good solid piece of charcoal, sufficiently large, should be selected, and bound with iron or copper wire, to prevent its breaking into pieces. It should then receive a coating of plaster, half an inch in thickness, on all sides except the one upon which the object to be soldered is to rest. This adds to its strength and protects the fingers from being soiled in handling it. Good charcoal, suitable for use in the dental laboratory, cannot, however, always be found

when wanted, and it is therefore often necessary to use some other substance which may be more easily obtained. Thus, those living in large cities may be compelled to employ pieces of coke as supports in soldering. Next to charcoal, coke is most suitable for that purpose. It is more durable than charcoal, and when such a support, composed of one large piece, or even several smaller pieces, is bound together with wire and coated with plaster, it will last a long time. Large pieces of pumice-stone also answer well for the purpose of holding small objects while the flame of the blow-pipe is directed upon them. Neither of these, however, is so well adapted as charcoal for holders when small quantities of metals are to be melted, in consequence of their greater porosity and hardness, which prevents the cutting of suitable pits for the reception of the metal to be fused.

A very good support for soldering purposes alone may be formed by filling a cup made of sheet iron or copper, five inches in diameter by five inches in depth, with a mixture of asbestos and plaster, or plaster and finely-broken charcoal. The vessel should be supplied with a wooden handle, fastened in the bottom for convenience in handling.

Plattner's "Manual of Qualitative and Quantitative Analysis with the Blow-pipe," page 15, gives a method of artificially preparing good solid supports of charcoal which might be found of value in the dental laboratory. It consists of mixing charcoal dust (which must not be too finely ground) with starch paste. The latter is prepared by combining one part of starch with six parts of boiling water.

These are stirred in an earthen pot until all the meal is converted into paste. This paste is rubbed in a porcelain mortar, with frequent additions of charcoal dust, until the mass becomes too tough for further admixture, when enough of the coal-dust is kneaded in with the hands to render the whole mass stiff and plastic. From this the desired forms of blow-pipe coals can be made, allowed to dry gradually and thoroughly, and then heated to redness in a covered vessel so as to char the starch paste. The charring may be regarded as complete when the evolution of gases from the mass ceases, or when it has been heated to dull redness. Coals thus formed are of the proper firmness, and ring like ordinary good charcoal when thrown on the table.

Blocks formed of graphite and fire-clay are now often used as supports for holding objects to be soldered, but they do not answer the purpose well, in consequence of not being sufficiently non-conducting, and they soon become so hot in the operation of soldering that it is impossible to hold one in the hand for any length of time.

When the object to be soldered is an artificial denture containing a number of teeth, a support that will be found to answer all requirements is the hand-furnace, such as is now furnished by the dental depots (see Fig. 18). It consists of a funnel-shaped receptacle of sheet iron, with a grate or perforated plate near the bottom, and a small door on one side underneath the grate for the admission of air. The upper part of the holder is surmounted by a cone-shaped top; to the bottom is attached an iron rod, five or six inches long, terminating in a wooden handle.



This apparatus is designed to serve both the purpose of heating the case and as a support or holder during the soldering. For the first it is not well suited, being too small to contain fuel enough to admit of a thorough heating of the case; but when the object to be soldered has been brought to the proper temperature, it makes a capital holder for a set of teeth

FIG. 18.



while the flame of the blow-pipe is being directed upon it. The best method of heating up a case is to place it on a gas-oven, such as is employed in the dental laboratory for general use and for heating flasks in packing rubber work, etc. A ring of cast or sheet iron, six inches in diameter by two inches high, should then be placed around it for the purpose

of holding the charcoal, which, in pieces the size of a hen's egg, should be built around the outside of the case, so that it may be uniformly heated. The cone or top of the apparatus just described may now be placed over it. The gas is then lighted, but the full head should not be turned on until the moisture of the investment has been driven off, when it may be gradually increased until the case is heated to redness. About thirty minutes will be required to reach the proper temperature for soldering, when the case may be lifted from the gas-oven with suitable tongs and placed in the hand-furnace. The live coals used in heating up should also be placed around the outside of the investment to prevent the too rapid cooling of the piece, should any delay in the soldering occur. When the latter operation has been satisfactorily completed, the top may be placed tightly on, and all access of air excluded, in order that the case may cool slowly and thus avoid the danger of cracking the teeth.

## CHAPTER VII.

### COMBINATIONS OF METALS WITH NON-METALLIC ELEMENTS.

THE metals combine with the non-metallic elements, to form a new class of bodies wherein none of the distinctive characteristics of the constituents are discernible. These are the

Chlorids,  
Bromids,  
Iodids,  
Fluorids,  
Cyanids,  
Oxids,  
Sulfids.

Metals also form definite compounds with nitrogen, phosphorus, silicon, boron, and carbon.

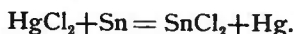
*Chlorids.*—All metals combine with chlorin, and some of them in different proportions, as illustrated by the stannous and stannic chlorids, the first having a formula of  $\text{SnCl}_2$ , while the composition of the latter is  $\text{SnCl}_4$ . The capacity of the metals for combination with chlorin is not uniform. The different proportions are designated by the following terms :

Monochlorids,	such as	KCl.
Dichlorids,	“	$\text{BaCl}_2$ .
Trichlorids,	“	$\text{AuCl}_3$ .
Tetrachlorids,	“	$\text{SnCl}_4$ .

The chlorids may be prepared by acting upon the metals with nascent chlorin developed by hydrochloric and nitric acids.\* Some chlorids, on the other hand, are formed by bringing a current of chlorin gas in contact with the metal. In this way titanitic chlorid is formed, the chlorin being passed over a heated mixture of charcoal and titanitic oxid. Aluminum and chromium chlorids may be similarly obtained.

The rationale of the action of chlorin upon metallic oxids is that it drives out the oxygen and unites with the respective metals to form chlorids. The interchange may take place at ordinary temperatures, as in the case of silver oxid, but in others an elevation of temperature (sometimes to red heat) is required.

Many metallic chlorids are prepared by acting upon the metals with hydrochloric acid. Zinc, cadmium, iron, nickel, cobalt, and tin dissolve readily in hydrochloric acid, with liberation of hydrogen. Sometimes a chlorid is obtained by substituting one metal for another. In this way stannous chlorid is frequently prepared by distilling metallic tin with mercuric chlorid, thus :



Lastly, a chlorid may be prepared by dissolving a metallic oxid, hydroxid, or carbonate in hydrochloric acid.

*Bromids.*—Bromin unites directly with most metals, and forms compounds analogous in composition and general properties to the chlorids. Sea-water and many of the saline springs contain native bromids,

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\* Aqua regia,—i.e., two volumes of hydrochloric with one volume of nitric acid.

and silver bromid occurs as a natural mineral. The affinity of bromin for the metals is inferior to that of chlorin, and the latter, with the aid of heat, drives out the bromin and converts the substances into chlorids.

*Iodids* are compounds possessing properties analogous to those of the chlorids and bromids, and are obtained by processes similar to those which yield the latter. With the exception of those of gold, silver, platinum, and palladium, they are not decomposable by heat alone.

*Fluorids* are compounds formed by heating hydrofluoric acid with certain metals, or by the action of that acid on metallic oxids. They may also be formed by heating electro-negative metals—antimony, for example—with fluorid of lead or fluorid of mercury. The fluorids are destitute of metallic luster, and most of them are easily fusible, and bear a close resemblance to the chlorids.

*Metallic oxids* may be variously formed. Some metals, by mere exposure to air while heated, lose their metallic character, and, by combination with oxygen, assume a totally different appearance.

There are several methods of forming oxids artificially, and some oxids are capable of being converted into others of a higher degree. Red lead, for instance, is thus formed, the metal being first heated without allowing it to fuse, when a protoxid of a yellow color is formed; but on further exposure to a temperature of  $315.5^{\circ}$  C., with free access of air, additional oxygen is taken up, and the mass assumes a brilliant red color.

Oxids of metals are also formed by heating a nitrate

or carbonate to redness, by which means the acid will be evolved while the oxid remains. Thus, a protoxid of lead may be formed by heating the white carbonate of the metal, its color soon changing to a lemon-yellow as the acid present is driven off.

Oxids of some of the metals—copper being an example—are formed by first acting upon the metal with nitric acid, and in that way obtaining a nitrate, which is dried and heated to dispel the acid, when the oxid will remain.

Again, if we deflagrate some of the metals with a body containing a large proportion of oxygen, we obtain their oxids. Tin, lead, zinc, etc., are in this way removed from alloys in which they enter as prominent constituents. For example, take, say, one gramme of an amalgam alloy, consisting of tin, silver, gold, and platinum, place it in a crucible and melt with borax. If crystals of potassium nitrate are then dropped into the fluid mass, the tin is converted into an oxid, and is dissolved and held by the borax glass. If this part of the process is thoroughly performed, the remaining button will be found to contain only the noble metals, silver, gold, and platinum, which may be easily separated and weighed, thus affording a very simple method of quantitative analysis for ascertaining the proportions of amalgam alloys.

Metallic oxids in the form of hydrates are obtained by treating an aqueous solution of a metallic salt with an alkali. Thus, the hydrated sesquioxid of iron, commonly employed as an antidote in arsenical poisoning, is produced by adding ammonia to ferrous sulfate. Zinc sulfate or cupric sulfate, by the addition of caustic potassa, yields bulky hydrated oxids.

These in turn may be converted into simple oxids by heat.

Superficial oxidation may occur gradually by mere exposure to air at ordinary temperatures, and the action will be accelerated by the presence of moisture. It frequently occurs, however, that metallic objects thus superficially oxidized are so protected by the newly-formed oxid from further access of air that oxidation can no longer go on ; but should the rusted or tarnished surface of an iron or leaden object be removed, oxidation will again occur.

Many metallic oxids are formed during fusion of the metals. Lead and zinc are examples of this. The former, by continued exposure to a sufficient degree of heat, may be entirely changed into an oxid, and the latter, when carried to a temperature much above its fusing-point, burns with a brilliant light, during which the oxid is evolved in the form of white fumes, the incandescence accompanying the combination being an evidence of the intense affinity which the metal at an elevated temperature has for oxygen. Other of the metals are thus combustible. The familiar experiment of converting iron into an oxid by throwing a jet of oxygen gas upon a red-hot bar of the metal is an illustration of the fact, and many metallic oxids may be thus formed by deflagration.

There are, however, a few noble metals possessing so feeble an affinity for oxygen that they cannot be made to combine directly with the latter ; even when the oxids of these are obtained by chemical means, the metals separate from the oxygen upon being heated to redness.\* Gold and platinum are illustra-

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\* See " Noble Metals."

tions of this class of metals. The latter, which is employed as a base-plate in the "continuous-gum process" and for pins in artificial teeth, is subjected to the most intense furnace-heat without the slightest oxidation of surface.

Many of the metallic oxids occur in nature, a number of the metals being reduced from natural ores, which are oxids of their respective metals, such as iron, tin, manganese, chromium, etc.

*Sulfids.*—The metals unite with sulfur and form a class of compounds which, in a chemical and economical point of view, are almost as important as the oxids. These were formerly termed sulfurets. Many of them are found as natural ores, and are generally brittle solids possessing a high metallic luster, the latter quality being so marked in some that they have been mistaken for gold. Sulfur combines with the metals in varying proportions, and it may be observed that combination takes place in proportions similar to the oxids, the only exceptions to this analogy being the alkalis and alkaline earths,—there being but two oxids of potassium, sodium, and barium, while there are no less than five sulfids of these metals.

All the metallic sulfids are solid at ordinary temperatures, most of them fuse at red heat, and some sublime unchanged. The admission of air to the heated sulfids is followed by their decomposition and conversion into sulfates, or, if they are exposed to higher and continued heat, into oxids. The sulfids are all insoluble in water, with the exception of those of iodine, potassium, strontium, barium, and calcium. The metallic sulfids may be artificially formed by the following processes: by heating the metals or their



oxids with sulfur;\* and from the sulfates by heating them with charcoal, or in a current of hydrogen by passing a stream of sulfuretted hydrogen through their solutions, or by adding to them a solution of an alkaline sulfid.

### REDUCTION OF METALLIC COMPOUNDS.

The term "reduction," as used in metallurgy, refers to the different methods of separating a metal from its natural ores or from combination with any non-metallic element. In some cases this is effected by heat alone. For example, the noble metals are separated from oxygen by merely heating to  $600^{\circ}$  F ( $=315.5^{\circ}$  C.) Generally, however, the joint action of heat and reagents for which the non-metallic constituents of the compound have greater affinity is required.

The inventions of Eugene H. and Alfred H. Cowles, of Cleveland, Ohio, and of Graetzel, near Bremen, in Germany, have proved to be a most important advance in metallurgy. The essential feature in the improvements of these gentlemen is the application of the intense heat of a current of electricity from a dynamo machine through a conductor of great resistance in the presence of carbon. Many of the most refractory ores, which have hitherto resisted all similar attempts, may be readily decomposed in these electrical furnaces. By this means aluminum is now reduced from corundum.†

The metallic compounds, whether natural or artifi-

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\* Silver is an example of this. So great is its affinity for sulfur that rubber, the indurating agent of which is sulfur, cannot be vulcanized in contact with that metal.

† See chapter on "Aluminum."

cial, are a class of bodies formed of dissimilar elements held together by the force of chemical affinity, and which are totally unlike either of their constituents. This affinity varies much in different metals. Thus, gold possesses very feeble affinities, and when combined with chlorin it may be partially precipitated by mere exposure to light or the atmosphere. The facility with which it often passes from one element to another may be observed in the interesting process of manufacturing "shredded gold,"\* in which an acid solution of the trichlorid is formed and slightly heated in a glass matrass; gum arabic or sugar dissolved in water is then added, when beautiful web-like masses of pure gold are seen to form in the liquid, but unless these are quickly removed by means of a glass spoon or dipper, they will almost instantly dissolve and the gold again unite with the chlorin. Lead, tin, zinc, iron, and many other metals evince stronger affinities; hence, they are not so readily reduced, and require, in addition to heat, the presence of other substances, such as coal, coke, charcoal, etc. In other words, it is necessary to expose them in contact with some reagent between which and the non-metallic constituents of the compound superior affinity exists, so that by union of these the metal may be released. Indeed, it may be truly said that all analytical operations for the reduction of ores and the discrimination and estimation of unknown bodies are performed by taking advantage of the different degrees of chemical affinity. Thus, lead which has been overheated or subjected to frequent or long-continued meltings becomes partially oxidized and covered with an earthy-looking mass

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\*"Lamm's shredded gold." See "Preparations of Gold."

consisting of semi-oxidized metal, formerly called the "calx." Further exposure to heat would simply have the effect of converting this into an oxid of a higher degree, but if covered with finely-broken charcoal, or other carbonaceous substance,\* the latter will extract the oxygen, carbonic acid will be formed and evolved, while the metal will be restored to a free state.

*Chlorids.*—With the exception of the chlorids of the metals of the alkalies and earths, all metallic chlorids are decomposed when heated in a current of hydrogen, hydrochloric acid and the pure metal being the result. The chlorids of gold and platinum are decomposed by simple ignition.

Argentio chlorid, when heated on charcoal, under the flame of the blow-pipe, yields pure silver and emits an odor of hydrochloric acid. Placed in water acidulated with sulfuric or hydrochloric acid, argentic chlorids may be reduced by the addition of pieces of some easily oxidized metal, such as zinc or iron, the rationale of the reaction being as follows: the zinc displaces the hydrogen of the  $H_2SO_4$ , zincic sulfate is formed, the liberated hydrogen unites with the chlorine to form hydrochloric acid, and pure silver remains.

Sulfuric acid decomposes the chlorids and converts them into oxids, the oxygen being supplied from the water present. Some chlorids may be decomposed by heating them with a metal which has more powerful basic properties. Thus, sodium, when heated with aluminum or magnesium chlorid, will become sodic

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\*In the dental laboratory beeswax is usually employed to deoxidize lead or zinc which has become thick and earthy by frequent meltings.

chlorid, with liberation of the magnesium or aluminum. Some chlorids are reduced by heating with a mixture of sodic carbonate and charcoal; other carbonaceous compounds, such as sodic or calcic carbonate, are frequently used.

*Sulfids.*—Reduction of the sulfids, in some few instances, such as those of gold, silver, and platinum, is effected by heat alone. The oxygen of the atmosphere unites with the sulfur, which is evolved as sulfurous acid. In many cases, however, a portion of the oxygen combines with the metal, and an oxid instead of the free metal is obtained. The reduction of many of this class of ores consists simply in such interchanges. The application of heat and air in some instances converts the sulfid into a sulfate, which in turn may be decomposed at high temperatures and separated into sulfurous acid and a metallic oxid. On the other hand, some of the sulfids may, when heated with access of air, be converted into permanent sulfates capable of resisting high degrees of heat. The sulfids of the noble metals, when heated, part directly with the whole of their sulfur, leaving the metal in a pure state. Silver sulfid thus reduced is also partially oxidized, so that a small portion of argentic sulfate is formed, which requires for its reduction a still greater elevation of temperature.

Reducing agents, such as metallic iron, hydrogen, chlorin, etc., are frequently employed to combine with sulfur. If sulfids of lead be heated with iron, sulfid of iron and metallic lead result. This method is frequently practiced in the assay of galena, clean iron nails being heated with the ore. The sulfids of antimony, bismuth, copper, tin, and silver are readily

reduced by passing dry hydrogen over them at red heat, the result of the reaction being the free metal and sulfuretted hydrogen, the product of the union of the hydrogen and sulfur. Dry chlorine will also decompose them, and combine with both the metal and the sulfur. Nitro-hydrochloric acid converts the sulfids into chlorids, and hydrochloric acid in a few instances acts similarly ; its hydrogen, combining with the sulfur, is evolved as sulfuretted hydrogen. Strong nitric acid also decomposes them, and is often employed in analyses of ores. The sulfur being thus oxidized, the liberated metal combines with the acid to form a nitrate, mercuric sulfid or native cinnabar being the only ore which cannot be thus reduced.

*Oxids.*—The reduction of lead, zinc, or tin, the working qualities of which have been impaired by frequent meltings with exposure to air, may be effected in the laboratory by placing the metal to be treated either in a large clay crucible or in the ordinary iron melting-pot employed by dentists. The semi-oxidized metal is then covered with powdered charcoal, when the reaction described above takes place, and the original properties of the metal are restored.

There are some oxids to which the foregoing treatment is not applicable, but these may be reduced by passing a current of dry hydrogen over them when heated to redness. Makins gives the following very clear description of this method of reducing oxids :

“ A large two-necked bottle is fitted up in the usual way for the evolution of hydrogen. This has its delivery-tube passed into a tube filled with fragments of calcic chlorid, for the purpose of absorbing the

moisture which may be carried over with the gas ; to the other end of this drying-tube is connected the tube which is to hold the metallic oxid (generally in a bulb blown upon this). The gas bottle should contain about a couple of quarts, so as to afford a steady supply, and the calcic chlorid tube should be long and well filled. In operating, after the gas has completely driven out the air in the apparatus, heat is applied to the bulb containing the oxid, and its reduction will be brought about. The gas must be kept up in a good stream, so as to drive out the watery vapor formed by the decomposition. Here the hydrogen takes the oxygen of the oxid, and water is formed, while the metal is set free."

There are metals whose affinity for oxygen is so strong that their union with that element cannot be broken up by such means as we have described. Deoxidation of these metals must be performed through the agency of some other metal possessing greater affinity for oxygen. For example, if oxid of iron be heated with potassium, the iron will be deoxidized, while the potassium will be converted into potash ( $K_2O$ ).

Some metallic oxids may be reduced by heating with sulfur, part of the latter abstracting the oxygen, with which it unites to form sulfurous acid. A portion of the sulfur, however, unites with the metal, which is converted into a sulfid, or a sulfate, or a mixture of both. These must then be treated according to the directions already given for the reduction of metals when combined with sulfur.

There are also a few metallic oxids which chlorin gas will reduce. Thus, platinum is liberated from

combination with oxygen when exposed to a current of dry chlorine.

Probably the most powerful means of reducing metals from combination with non-metallic elements is that known as electrolysis. It consists in exposing a solution of a metallic salt to the decomposing influence of the galvanic current. A demonstration of this force may be made by taking a solution of nitrate of lead (plumbic nitrate) and immersing in it a piece of zinc. The latter soon becomes covered with needle-like crystals of pure lead; the zinc replaces the lead, which is set free and deposited at the point of galvanic action. Or, the same phenomenon may be witnessed by immersing a piece of clean iron in a solution of copper, or a piece of copper in a solution of a salt of mercury,\* the action only ceasing when all the metal in the solution is reduced.

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\* Reinsch's test for the detection of the mineral poisons is based upon this principle.

## CHAPTER VIII.

### GOLD.

ATOMIC WEIGHT, 197. SYMBOL, AU (AURUM).

**G**OLD is one of the few metals which is found in the metallic state, and it was probably one of the first known to man. Allusions to it are frequent in the Old Testament, and jewelry and vessels found in Egyptian tombs afford evidence of the perfection attained in working it at a period earlier than the government of Joseph. There are many evidences that processes of alloying, refining, and separating gold were practiced at a very early period of the world's history. According to Pliny, the metallurgy of gold was known in his day. Vitruvius also gives a detailed account of the method of recovering gold by amalgamation from cloth into which it had been woven. It was employed in Rome for the purpose of fixing artificial teeth more than three hundred years before the Christian era, and a law of the "Twelve Tables" makes exception with regard to such gold, permitting it to be buried with the dead.\* The great beauty of color and luster, and the power of resisting oxidation which gold possesses, have caused it to be valued from the earliest ages for the purpose of adornment, and as a circulating medium.

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\* Phillips's Metallurgy.



*Occurrence, Distribution, and Properties.*—Gold is of nearly universal distribution, and is found in nature chiefly in the metallic state as native gold. It occasionally occurs in combination with tellurium, lead, and silver, forming a peculiar group of minerals, confined to a few localities in Europe and America, these being the only certain examples of natural combinations of the metal. The most important minerals containing gold are sylvanite or graphic tellurium,  $(\text{AgAu})\text{Te}_2$ , containing about twenty-four per cent. of gold; calaverite,  $\text{AuTe}_2$ , containing about forty per cent. of gold, and nagyagite or foliate tellurium, the composition of which is not definitely known. It contains from five to nine per cent. of gold. The metallic sulfids, such as galena and iron pyrites, usually contain sensible quantities of gold, the lead ore being almost invariably gold-bearing. Native arsenic and antimony also occasionally contain gold, and a native gold amalgam has been found in California.

Gold occurs in nature very nearly though never quite pure, being generally associated with silver. Other metals are occasionally found combined with it, but in very small quantities; and these foreign metals are peculiar to localities. Thus, California gold, in addition to silver, which is always present, may contain iridium; Russian gold often contains platinum, and specimens of the native metal from Brazil will not infrequently be found to contain palladium.

## Analyses of Native Gold from Various Localities.

	Gold.	Silver.	Iron.	Copper.
UNITED STATES :*				
California	90.12	9.01	6.15	
EUROPE :				
Vigra & Clogau .	90.16	9.26	trace.	trace.
Wicklow (river) .	92.32	6.17	0.78	
Transylvania .	60.49	38.74		0.77
ASIA :				
Russian Empire—				
Brezovsk	91.81	8.03	trace.	0.09
Ekaterinburg	98.96	0.16	0.05	0.35
AFRICA :				
Ashantee	90.05	9.94		
AMERICA :				
Brazil	94.0	5.85		
Central America .	88.5	11.96		
Titiribi	76.41	23.12		0.87
Cariboo	84.25	14.90		0.03
AUSTRALIA :				
South Australia .	87.78	6.07	6.15	
Ballarat .	99.25	0.65		

Pure gold is of a rich yellow color, and is nearly as soft as lead. It is, with one exception (platinum), the heaviest substance in nature, being about nineteen and a half times as heavy as water. These properties are all sensibly modified by admixture of other metals. Thus, the tint is lowered by small quantities

\* The yield of gold in the United States in 1876 was greatly in excess of that of any other country on the globe, Russia being next in quantity produced.

of silver, and heightened by copper. Owing to its exceeding softness, gold is commonly used alloyed, in order to render it capable of resisting the attrition to which coins and articles of jewelry are exposed. It is the most malleable of all the metals. One grain may be beaten into leaves which would cover a surface of fifty-six square inches, and only  $\frac{1}{800000}$  of an inch thick.\*

Very thin gold leaf appears yellow by reflected and green by transmitted light. Highly attenuated films of gold, when heated, transmit rays of light of a ruby-red color. The pressure of a hard substance on the film will, however, so change its state of aggregation that the green color will again appear.

Gold is exceedingly ductile, but does not possess a very considerable degree of tenacity. A grain of gold, however, if covered by a more tenacious metal, such as silver, may be drawn into a wire five hundred feet in length. It also possesses the remarkable property of welding cold. Thus, the metal, in the state in which it is obtained by precipitation by oxalic acid, may be formed into disks or medals by compression between dies.

The specific gravity of gold varies according to condition. In the finely divided state in which it is obtained by precipitation by oxalic acid it is 19.36. The specific gravity of cast gold is somewhat less, but when compressed between dies, or by the rolling-mill, it may be raised from 19.37 to 19.41. Annealing, however, will restore its previous density to nearly that of the cast metal.

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\*The late Dr. S. S. White presented the author with a specimen, securely mounted between plates of glass, which is but  $\frac{1}{800000}$  of an inch in thickness. It is transparent, and transmits green rays of light.

The atomic weight of gold has been variously stated. Berzelius gave it as 196.67 ; Levol, 196.3 ; Wurtz, 196.5 ; Watts, 196.0 ; Bloxam, 196.6 ; Fownes, 197. There seems also to be a similar diversity of opinion regarding the temperature at which it fuses. Thus, Daniell fixed the melting-point at  $1425^{\circ}$  C. ; Pouillet,  $1200^{\circ}$  C. ; Guyton de Morveau,  $1380^{\circ}$  C. The figures,  $1102^{\circ}$  C., given in Fownes's "Elementary Chemistry," are probably as nearly correct as any, and for all practical purposes will answer very well.

The electric conductivity of gold is given by Matthiesen as 73.96 at  $15.1^{\circ}$  C., pure silver being 100. The conducting power, however, depends much upon the degree of purity, as the smallest addition of another metal will very considerably lower its conductivity.\*

The conductivity of gold for heat is stated as 53.2, as compared with pure silver, 100. Its specific heat is 0.0324.

*Volatility.*—The absence of uniformity in results of experiments with regard to this property given by different investigators would seem to leave the matter still in doubt. Thus, Gasto Claveus and Kunkel describe similar experiments, wherein an ounce of pure gold was placed "in an earthen vessel in that part of a glass-house where the glass is kept constantly melted, and retained in a state of fusion for two months, without the loss of the smallest portion of its weight." On the other hand, Homburg, Lavoisier, and Maquer state that when a small portion of gold is kept at a violent heat part of it is volatilized, and that a piece of silver held in the rising fumes will have its surface gilded. It is quite prob-

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\* See "Power of Conducting Electricity."

able that, when a small portion of gold is mixed with a large quantity of zinc and heated in the air, the whole of the gold will be dissipated with the fumes of oxid of zinc. Mr. Makins has demonstrated that gold, silver, and lead, when cupelled together, volatilize. Gold may also be volatilized, when in the form of leaf or highly-attenuated wire, by passing a powerful charge of electricity through it.

*Forms of Native Gold.*—The native metal is sometimes found in the form of cubic crystals, in octahedra, and in irregular and more complex shapes called nuggets and dust. Crystals of gold may also be obtained artificially from an amalgam of gold one part, mercury twenty parts. The mixture is maintained at a temperature of 80° C. for eight days. The mercury is then removed by strong nitric acid, leaving crystals of gold, which require to be heated to redness to develop brilliancy of surface.

Gold is found in quartz veins or reefs traversing slaty or crystalline rocks, alone or associated with iron, copper, magnetic and arsenical pyrites, galena, specular iron ore, and silver ores, and more rarely with sulfid of molybdenum, tungstate of calcium, bismuth, and tellurium minerals. It is also found among the detritus of disintegrated rock,\* associated with the metals of the platinum group. In the superficial alluvial or "placer" deposits it has been remarked that the minerals with which it is found intermixed are of great density and hardness, and are the most durable constituents of disintegrated rock.

The yield of gold in easily-worked alluvial deposits

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\* In the form of small lumps called "dust."

is often exceedingly small. It is stated that in the Siberian gold-washings the proportion of gold ranges from 12 grains to 1 dwt. to the ton of sand, while in the lodes which require more labor to work the proportion is but 8 dwts. per ton, and in the "placer" washings of California it is but 12 grains to the ton of gravel. In Australia the alluvial washings of Victoria yielded 25 grains to the ton. Vein mining being more difficult and costly, necessitates a larger yield of the precious metal, and 5 dwts., or about five dollars' worth of the gold, is in most gold-bearing localities regarded as a paying quantity.

The method of obtaining gold from alluvial deposits is exceedingly simple, and consists in washing away the lighter portions, leaving the heavy metallic particles. In the early days of gold-mining in California this was accomplished by means of a pan of sheet iron, thirteen or fourteen inches in diameter, held in the hand and its contents exposed to a stream of water; and on the large scale consists of washing the alluvial deposits into sluices or troughs by means of continuous streams of water,—mercury or amalgamated copper plates being sometimes employed to collect the finer particles of gold.

In vein mining the separation of the gold from the rock with which it is mechanically mixed consists in reducing the latter to a fine powder in grinding- or stamping-mills, and the gold is recovered by amalgamation, or by washing the pulverulent mass through troughs lined with coarse woolen cloths, by which means the lighter deposits are carried away with the current, while the heavier metallic particles become entangled in the fibers of the blanket until the surface

of the latter is completely covered, when it is removed and its contents are washed off in a suitable vessel and reserved for amalgamation.

In the treatment of gold by amalgamation the process is frequently retarded by a difficulty known as the "sickening" or "flouring" of the mercury. The latter, losing its bright metallic surface, is no longer capable of coalescing with other metals. The discovery was made by Wurtz, in 1864, that by the addition of a small quantity of sodium to the mercury the operation is greatly facilitated, the addition of the sodium preventing both the conditions above referred to which are produced by certain associated minerals. Some metallurgists recommend the addition of 20 per cent. of zinc and 10 per cent. of tin. It has been estimated that mercury will dissolve from 0.05 to 0.08 per cent. of native gold of standard 650 to 850 without loss of fluidity. The solubility of the gold increases with its fineness. When the point of saturation has been reached, lumps of the solid amalgam are introduced into an iron vessel lined with a mixture of fire-clay and wood-ashes, and provided with an iron tube, by which the fumes of mercury are passed through water and condensed, the distillation being effected at a temperature below redness. The gold left in the retort is then melted in a suitable crucible.

Gold is sometimes reduced from the mineral by exposing the ore, which has been previously roasted, to a current of chlorine gas. By this means the gold is converted into a soluble chlorid, which is removed by washing with water. The precious metal is then recovered in the metallic form by precipitation with ferrous sulfate. This process is, when carefully per-

formed, a very accurate one, and yields 97 per cent. of the gold present in the ore.

*Refining Gold.*—Methods of refining gold were known and practiced in very ancient times, and many of them, though empirically employed, did not materially differ in principle from those in use at the present day. Thus, in Strabo's time the gold was placed on the fire with three times its weight of salt and a quantity of argillaceous rock, which in the presence of moisture effected the decomposition of the salt. Hydrochloric acid is thus formed, which, at the high temperature employed, furnishes chlorine to the silver associated with the gold, which is converted into a chlorid. A similar process is still practiced in South America.

Among other methods for the separation of gold from silver or other contaminating metals, which have been in use from a remote period, may be mentioned prolonged oxidation by exposure to air, and melting with sulfur, sulfid of antimony, and corrosive sublimate.

The old "quartation" process of refining, so called from the fact that an alloy is formed, four parts of which contain three parts of silver and one of gold, consists in first forming an alloy of the gold with silver in the proportions given. These are melted to insure homogeneity, and granulated\* by pouring into water contained in a wooden vessel. The pieces are then collected and placed in a glass or platinum vessel, and acted upon by either nitric or sulfuric acid. When the presence of lead or tin is suspected, these

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\* Granulation is usually repeated twice or thrice.



should be got rid of before subjecting the alloy to the acid; otherwise the platinum digester would be injured. The removal of lead is accomplished by cupelling the alloy, while tin may be effectually removed by fusing the alloy with potassium nitrate. On account of greater economy and the closeness with which it will act upon silver containing very small quantities of gold, sulfuric acid is at the present day the agent most commonly employed, particularly where large quantities of the alloy are to be treated.

The nitric acid plan does not, as a rule, yield gold of as high a degree of fineness as the sulfuric acid treatment, but the oxidizing property of the nitric acid is of great advantage in refining gold contaminated with antimony and other equally injurious metals.

When nitric acid is employed, each ounce of the granulated alloy is treated with an ounce and a quarter of nitric acid of specific gravity 1.32.

The sulfuric acid process is based upon the facts that the concentrated hot acid converts silver and copper into soluble sulfates without attacking the gold, the metallic silver being recovered from the sulfate in the form of needle-like crystals by thrusting copper plates\* into it. The sulfate of copper resulting from the reaction is crystallized and becomes an article of commerce. The sulfuric acid should be of specific gravity 1.84, and the alloy is boiled for three or four hours in a platinum vessel with 2.5 times its weight of acid. The sulfurous acid fumes which arise are partially condensed before being allowed to pass into the air. When the acid has ceased to act upon the metal,

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\* Iron plates are sometimes used.

a small quantity of sulfuric acid of specific gravity 1.53 is added, and after a second boiling the contents of the vessel are allowed to settle ; the liquid is withdrawn from the gold, which rests at the bottom of the vessel, and is diluted until its density is 1.21 to 1.26. The gold is then carefully washed and melted into ingots, which generally contain from 997 to 998 parts of gold in the 1000.

In the nitric acid process the supernatant liquid consists mainly of argentic nitrate. The silver may be recovered by precipitation with chlorid of sodium, argentic chlorid resulting, which in turn is exposed to a current of hydrogen, liberating metallic silver.\*

The dry method of refining gold before alluded to consists in placing the granulated alloy and a mixture of one part of chlorid of sodium and two parts of brick-dust in alternate layers in a crucible until the latter is full, when it is covered and placed in a wood fire and kept at a dull redness for twenty-four hours. By the united action of the moisture furnished by the wood and the silica of the brick-dust the sodic chlorid is decomposed ; its sodium combines with oxygen from the decomposition of the water, forming soda, which in turn unites with silica to form sodic silicate. The hydrogen of the water and the liberated chlorin form hydrochloric acid ; these, at the temperature at which the operation must be carried on, furnish chlorin to the silver, converting it into argentic chlorid. The latter, being fusible, is absorbed by the brick-dust, permitting the alloy to be further acted upon, until nearly all the silver is converted into chlorid, the gold remaining comparatively free.

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\* See chapter on "Silver."

There is also another cementation process given,\* for the purpose of acting upon the surface of gold containing a large percentage of silver, by which means it is made to resemble fine gold. It consists in subjecting the alloy, previously rolled thin and covered by the cement-powder, to a temperature slightly below its melting-point. In this operation the mixture is composed of one part of sodic chlorid, one part of alum, one part of ferrous sulfate, and three of brick-dust. At the high temperature necessary the sulfates are decomposed, with liberation of free sulfuric acid, while chlorin is evolved from the sodic chlorid. These act upon the silver, which is subsequently found in the cement-powder in the form of argentic chlorid.

Refining by chlorin gas, devised by F. B. Miller, of Sydney, N. S. W., in 1867, is a valuable and accurate dry method for separating silver from gold. The process is the one now practiced in the Australian mints, where it has been quite extensively employed, 1,100,000 ounces of gold having been refined by it in Sydney during one year, the percentage of loss during the operation being only 14 parts in the 100,000. It consists in converting the silver into chlorid by the passage of a stream of chlorin gas through the molten alloy. By means of a clay pipe passing through the cover to the bottom of the crucible, and connected with the chlorin-generator by means of a flexible tube, the gas is passed rapidly through the melted metal, and is apparently absorbed by it. The refining is considered as complete when orange-colored fumes begin to rise. As soon as this

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\* This process is attributed to Kerl, and is described in Makins's *Metal-lurgy*, p. 224.

evolution of gas is noticed the crucible should be removed from the fire, to prevent the gold itself from combining with the chlorin. The chlorid of silver, which is fusible, should be poured off from the surface of the molten metal, and, if it retains a small portion of the gold, this may be recovered by fusing with a little carbonate of soda, which causes the gold to separate and settle to the bottom of the crucible. This method is capable of producing gold of from 944 to 1000 fine.

The gold is next melted into bars, and the argentic chlorid is reduced to metallic silver, by placing it between two wrought-iron plates, and then immersing the whole in a vessel of water acidulated with sulfuric acid, when, after a few hours, the silver will all be reduced. It generally, however, contains a small percentage of gold, which may be recovered either by again dissolving the silver with nitric acid, when the gold will be found at the bottom of the vessel; or it may be separated by fusing the argentic chlorid, to which is added a small quantity of potassic carbonate for the purpose of reducing a little metallic silver. The latter, in subsiding through the argentic chlorid, reduces the gold, which was probably combined with the chlorin. While yet hot and in a fluid state, the argentic chlorid is poured off and reduced as before, when it will be found free of gold. The little button which subsides to the bottom of the vessel will be found to consist of gold, the reduced silver, and some adherent argentic chlorid. The latter must be again decomposed by fusing with potassic carbonate. Theoretically, one cubic foot of chlorin will convert eight and a quarter ounces of silver into argentic chlorid,

but in practice about twice that quantity is required. Thus far the use of chlorin for refining upon a large scale has proved to be much more economical and expeditious than the humid process, the time required to part three hundred ounces in one furnace being about two hours, and the average cost four cents per ounce.

*Treatment of Brittle Gold.*—The slightest admixture of such metals as arsenic, antimony, tin, lead, etc., is sufficient to seriously impair the ductility of gold. In 1856 the coining operations of the mint of England were much embarrassed by the importation of brittle gold, in which the contaminating metal did not exceed the  $\frac{1}{1920}$  part of the mass. To purify the gold it was exposed while in a state of fusion to a stream of chlorin gas, which removed the deleterious substances by converting them into volatile chlorids. The toughness of gold may also be restored by throwing a small quantity of corrosive sublimate on the surface of the molten metal, the vapor of which converts the metallic impurities into chlorids, which are volatilized. In the dental laboratory gold is liable to become contaminated with small particles of lead or zinc. These may be effectually removed by melting with a mixture of potassium nitrate and borax, when the foreign metals will be oxidized and dissolved in the slag. Another process consists in adding to the melted mass about 10 per cent. of black oxid of copper. But this plan is objectionable, because the crucible is liable to become much corroded, and even perforated, and the standard fineness of the gold lowered, by a portion of the copper being reduced to the metallic state.

The gold of this country is often found to contain

iridium, the presence of which greatly impairs the metal for coinage and other purposes. The little hard grains occasionally met with in gold, upon which the file makes no impression, consist of iridium, or a native alloy of osmium and iridium, and are not combined with the gold, but merely disseminated through it. The only dry method of separating iridium from gold consists in alloying the latter with three times its weight of silver, by which means the specific gravity of the metal is so much lowered that the iridium, which is very infusible and of a specific gravity of 21.1, will subside to the bottom of the crucible, when the gold and silver alloy may be poured or ladled off. As some gold will remain with the residue, more silver must be melted with it, the operation being repeated several times, until all the gold is removed. What is left is then acted upon by sulfuric acid to dissolve the silver, when the iridium and some finely-divided gold will be left. These may be separated by washing.

Iridium may also be separated from gold by the wet process. The gold is melted with three times its weight of silver, and granulated to insure admixture. The alloy is then treated with nitric acid, which dissolves the silver, leaving the gold and iridium at the bottom of the vessel. The gold may now be acted upon by nitro-hydrochloric acid. The iridium may then be collected and washed to free it from any portion of the gold. The latter may be recovered from its solution by precipitation, oxalic acid or sulfurous acid being usually employed.

*Preparation of Chemically-Pure Gold.*—None of the methods which have been described can always be relied upon to afford absolutely pure gold. When

nitric acid is employed in the quartation process, gold may be obtained from 993 to 997 parts in the 1000, while sulfuric acid will frequently yield gold up to 998 thousandths.

Assays made by Messrs. DuBois and Eckfeldt, assayers at the United States Mint, of some of the most prominent foils give the following results :\*

No. 1. Abbey's Non-cohesive	998.8	998.7
“ 2. Wolrab's	999.2	999.3
“ 3. Quarter Century, S. S. W. Dental Mfg. Co.	999.1	999.1
“ 4. Rowan's Decimal foil	999.9	999.8

There are several methods by which chemically-pure gold may be obtained. Usually, ordinary refined gold, obtained by one of the methods above described, is dissolved in nitro-hydrochloric acid. The excess of acid is driven off, and alcohol and chlorid of potassium are added for the purpose of precipitating platinum, if any is present. The chlorid of gold is then dissolved in pure distilled water, until each gallon does not contain more than half an ounce of the chlorid. Any silver present will be converted into argentic chlorid, which will settle to the bottom of the vessel, after which the supernatant liquid should be carefully removed by means of a syphon. The gold may be precipitated by a stream of carefully-washed sulfurous anhydrid, or by the addition of oxalic acid. The precipitated metal is washed with dilute hydrochloric acid, distilled water, ammonia water, and again with distilled water, and is then ready for melting. This is done in a clay crucible, with a small portion of bisulfate of potash and borax. The melted metal should

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\* American System of Dentistry.

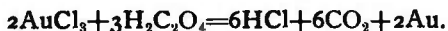
be poured into a stone ingot-mold. By this method gold, of which the purity was 999.96, has been prepared, the precipitant being oxalic acid; but gold precipitated by that agent from an acid solution containing copper is always contaminated with cupric oxalate, to avoid which the solution should be heated, with the addition of potash, when a soluble double oxalate of copper and potash is formed, leaving the gold in the pure state.

The aqua regia used in the preparation of chemically-pure gold should consist of two parts of hydrochloric and one part of nitric acid. The specific gravity of the former should be about 1.16, and of the latter 1.45. Each ounce of gold will require for its solution about three and one-half ounces of the mixed acids. The action of this upon the metal will in the beginning be quite energetic, but as the solution approaches saturation the application of moderate heat is required to dissolve the last portion of the gold. The greatest care must be exercised in the separation of the gold solution from the argentic chlorid, which subsides to the bottom of the vessel, and also to rid the liquid of the small portion of silver held in solution by the acid. The solution is cautiously transferred to an evaporating dish by means of a syphon, and heat is applied, and as the bulk is gradually reduced by evaporation more argentic chlorid will be separated and deposited at the bottom. The supernatant liquid should again be carefully poured or syphoned off, and this should be repeated as often as the residue appears in the dish. When the solution has become viscid and of a deep-ruby color, the heat is discontinued, and the auric chlorid soon crystallizes in a mass of prismatic forms.



It should then be dissolved and largely diluted with distilled water, acidulated by a few drops of hydrochloric acid, and, after standing for a few days to permit a further subsidence of argentic chlorid, it should be filtered, when it is ready for precipitation. This may be accomplished by quite a number of different reagents, but the form of the precipitated metal depends upon the nature of the precipitant, and it may be thrown down in a spongy condition, in sheets resembling foil, as a powder, in a more or less crystalline state, and in scales. The affinity of gold for other bodies is so weak that care must be observed lest partial reduction be effected by merely adventitious conditions. The highly diluted neutral solution of the trichlorid just described is quite liable to such accidents; indeed, it may occur from exposure to air, atmospheric nitrogen probably being the active agent. The addition of pure water to such a solution may also cause slight precipitation, but the dilute solution may be protected from premature precipitation by acidulation with a small quantity of hydrochloric acid.

The best agents for the precipitation of gold are oxalic acid, sulfurous acid, and ferrous sulfate. Oxalic acid will precipitate several forms of gold, from sponge-like masses to the different crystalline or powdery forms. Its action is, however, slower than the others, and it requires to be slightly heated. The reaction is shown in the following equation:



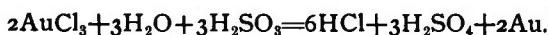
The chlorine of the auric chlorid unites with the hydrogen of the oxalic acid to form hydrochloric acid, the copious evolution of gas noticed during the precipitation being the escape of the carbonic acid formed

by the remaining elements of the oxalic acid. The gold is thus set free.

The so-called "shredded gold," somewhat extensively used by dentists in filling teeth during 1867-68, was produced by the addition of sugar or gum arabic to an acid solution of gold. The exact *modus operandi* is as follows: The pure gold is dissolved in nitrohydrochloric acid, and, without evaporating the solution, it is diluted by the addition of about two-thirds its bulk of pure water. Clean gum arabic, dissolved in boiling water to the amount of one-third the bulk of the gold solution, is added to the latter, and the whole poured into a glass matrass or evaporating-dish and placed over a steam bath. When the proper temperature is attained, gold in the form of leaves, shreds, or fibers will be observed floating in the liquid. When these become sufficiently coherent to admit of removal they are lifted out by a vulcanized rubber spoon attached to a glass rod, and placed in a filter. This operation is continued until the gum arabic or sugar, assisted by heat, has caused the precipitation of all the gold held in solution. The web-like masses are then thoroughly washed, dried, and heated to dull redness. As the elements entering into the composition of sugar and gum arabic are identical with those of oxalic acid, the reaction is probably the same as that which occurs when the latter is employed as the precipitant. With care in the application of the proper amount of heat, the action of precipitants of this class is capable of regulation, thus affording uniform results.

When the precipitated gold is intended for plate or bars, it should be well washed, and fused in a perfectly new crucible.

Sulfurous acid precipitates gold generally in the form of a scaly metallic powder; hence it does not afford masses sufficiently coherent or sponge-like for use as a filling-material for the dentist. The reaction which takes place is thus explained:



The water present is decomposed, its hydrogen uniting with the chlorine of the auric chlorid to form hydrochloric acid. The oxygen of the water, attracted to the sulfurous acid, converts it into sulfuric acid, and the gold is thus liberated.

Ferrous sulfate precipitates gold in the form of a light-brown powder. Of the sulfate crystals about four times the weight of the gold is dissolved in water. This is added to the auric solution. After the finely-divided gold has entirely subsided, it should be boiled several times in dilute hydrochloric acid, in order to free it from all traces of the iron with which it is liable to be contaminated. The interchange, which in this reaction results in the liberation of the gold, is expressed by the following equation:



The ferrous salt parts with a portion of the iron to the chlorine of the gold salt, thus forming ferric chlorid and ferric sulfate, while the gold is liberated.

As stated before, the reduction of the metal from the trichlorid may be effected (in, however, a less satisfactory manner) by many different reagents, some of which are purely elementary. Thus, sulfur, selenium, carbon (charcoal), and phosphorus, each, when introduced into a heated solution, becomes coated with a film of metallic gold. Reduction may also be

accomplished by some of the gaseous bodies containing hydrogen. Thus, gold may be precipitated by arseniureted and antimoniuureted hydrogen. Many of the base metals, such as bismuth, zinc, etc., also reduce gold from solution in the form of a brown powder. It is also reduced on a platinum pole by the electrical current. In this way the beautiful form of gold made by A. J. Watts, of New York, is produced. In a solution of auric chlorid plates of pure gold are suspended. These are connected with a battery, so that as the solution loses its gold by deposition of the metal it is re-supplied from the suspended plates. By this means large masses of perfectly pure crystal gold may be obtained.

Gold may also be precipitated by some of the metallic salts, of which nitrate of mercury and chlorid of antimony may be named as examples. Quite a number of organic substances will also precipitate it, a prominent example of which is gallic acid. The tartrate, citrate, and acetate of potassium will also reduce it. Some of the members of this class, however, require the addition of heat, and to obtain prompt action with these agents the solution should be quite neutral.

*Alloys of Gold.*—The most important alloys are those with silver and copper. The coinage of the present day, from which the dentist usually obtains his plate, is mainly an alloy of gold and copper, in the proportion of 900 parts of gold in 1000. Gold coins were first introduced in England by Henry III, in 1257. They were of pure gold. Edward III, in 1345, established a standard of 994.8, and in 1526 Henry VIII issued crowns of the double-rose, of the

standard 916.6. In 1544 the standard of all gold coins was reduced to 916.6, and again in 1548 to 833.4. Mary restored the old standard, 994.8. In Elizabeth's reign coins of both standards (916.6 and 994.8) were issued. In America the standard of gold coin is 900.

Alloys of gold for bases for artificial dentures should be of such fineness as will enable them to resist chemical action of the fluids of the mouth, while at the same time they should possess the requisite hardness, strength, and elasticity. These properties are usually conferred by the addition of copper and silver, or either of these metals singly; or by copper, silver, and platinum. The quality of gold which is to be introduced into the mouth should, as a rule, be of a standard of fineness not less than eighteen carats. Care, however, should be observed in remelting the scraps and filings of the drawer, that the grade of the gold be not lowered by the admixture of old plates, backings, etc., containing portions of solder. Indeed, much the safer rule is to remelt only new scraps, on which no solder has been used. The scraps and filings of doubtful quality may be sent to the mint for coinage, the charge for which, on the one hundred dollars (the minimum amount received by the United States Mint), is less than 1 per cent.

Gold exceeding nineteen carats in fineness will generally be found too soft and yielding for use in the mouth. The amount of force which the plate must sustain in mastication is much greater than might be supposed; hence, if the degree of purity of the alloy be too high, the requisite amount of rigidity and strength will be wanting, and the plate will soon bend

to such an extent that it will no longer fit the mouth. This difficulty may, however, be avoided in the higher grades of gold plate intended for dental purposes by a slight admixture of platinum, by which much greater tenacity is obtained ; otherwise the plate will require strengthening by doubling at such points as are most liable to bend. Plates for partial cases necessarily require a great deal of strengthening. This adds considerably to the expenditure of time and labor in the construction of the plate. It increases its weight, and does not always render the plate sufficiently rigid to withstand the force of mastication.

Gold plate suitable for dental purposes may be prepared according to the following formulæ, from Richardson's "Mechanical Dentistry :"

## Gold Plate 18 Carats Fine.

No. 1.		No. 2.	
Pure Gold	18 dwts.	Gold Coin	20 dwts.
Pure Copper	4 "	Pure Copper	2 "
Pure Silver	2 "	Pure Silver	2 "

## Gold Plate 19 Carats Fine.

No. 3.		No. 4.	
Pure Gold	19 dwts.	Gold Coin	20 dwts.
Pure Copper	3 "	Pure Copper	25 grs.
Pure Silver	2 "	Pure Silver	40+ grs.

## Gold Plate 20 Carats Fine.

No. 5.		No. 6.	
Pure Gold	20 dwts.	Gold Coin	20 dwts.
Pure Copper	2 "	Pure Copper	18 grs.
Pure Silver	2 "	Pure Silver	20+ grs.

## Gold Plate 21 Carats Fine.

No. 7.		No. 8.	
Pure Gold	21 dwts.	Gold Coin	20 dwts.
Pure Copper	2 "	Pure Silver	13+ grs.
Pure Silver	1 dwt.		

## No. 9.

Gold Coin	20 dwts.
Pure Copper	6 grs.
Pure Platinum	7 $\frac{3}{4}$ grs.

Gold Plate 22 Carats Fine.

## No. 10.

Pure Gold	22 dwts.
Fine Copper	1 dwt.
Pure Silver	18 grs.
Pure Platinum	6 "

Gold Plate 18 Carats Fine.

## No. 11.

United States Gold Coin (\$60)	64 $\frac{1}{2}$ dwts.
Pure Silver	13 "

On account of its greater strength and power of resisting chemical action of the fluids of the mouth, many dentists prefer to use gold plate twenty or twenty-one carats fine, in which the reducing constituents are copper and platinum, the following formula being an example :

Gold Coin	20 dwts.
Pure Platinum	10 grs.

The union of platinum with gold yields an alloy possessing great strength and considerable elasticity. Such an admixture, however, has its disadvantages. Owing to its increased strength and stiffness, a much thinner and lighter plate may be employed without the additional labor and cost of doubling the plate at what, in partial cases composed of ordinary 18-, 19-, or 20- carat gold, would be weak points. It may also be justly claimed for gold alloyed with platinum that it will perfectly resist the action of the fluids of the mouth. On the other hand, the richness of color of the

gold is always more or less impaired by the admixture of platinum. But perhaps the greatest objection to be urged against the employment of platinum-gold is the increased difficulty of swaging a plate composed of it so that it shall perfectly conform to all the depressions and irregularities of the model. Having invariably found, when the alloy contained any considerable percentage of platinum, that the ordinary method of swaging between zinc and lead was not effective, the author has for more than twenty years employed zinc for counter-dies as well as for dies ; this entirely overcomes any difficulty in swaging.\*

Gold for use in the formation of clasps should always contain sufficient platinum to render it much more elastic than the alloys usually employed in the plate or base, so that on the application of force upon the denture in the act of mastication the clasp, though it may yield slightly, will always spring together again and accurately embrace the tooth which it surrounds. In the perfect adjustment of clasps to remaining teeth the following points are of importance: First, the model must be as accurate as a plaster impression will afford ; second, the clasp should be thrown around the thickest or most prominent part of the tooth ; third, the clasp should be so arranged as to fit accurately the convexity of the tooth. To successfully accomplish this the gold, of about No. 26 of the standard gauge, should be cut by pattern, and before any attempt is made to fit it to the tooth it should be bent with the clasp-benders to correspond with the rounded surfaces of the natural tooth. Lastly, the contact of the clasps with the tooth should be uniform.

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\* See chapter on "Zinc."



The ends of the clasp should be free, and it should be attached to the plate at one point, so that but little of its circumference shall be included in the union ; otherwise, if a large proportion of the clasp be soldered fast to the plate, much of the quality of elasticity will be lost.

The following formulæ will afford alloys of twenty carats' fineness, suitable for clasps, backings, etc., whenever elasticity and additional strength are required :

Formula No. 1.		Formula No. 2.	
Pure Gold	20 dwts.	Coin Gold	20 dwts.
Pure Copper	2 "	Pure Copper	8 grs.
Pure Silver	1 dwt.	Pure Silver	10 "
Pure Platinum	1 "	Pure Platinum	20 "

*Alloys of Gold employed in Dentistry as Solders.*— These are a class of alloys formed of the metal to be united, the fusing-point of which is reduced by the addition of silver, copper, and brass.\*

No. 1. 14 Carats Fine.		No. 2. 14 Carats Fine.	
American Gold Coin, \$10.00		American Gold Coin, 16 dwts.	
Pure Silver	4 dwts.	Pure Copper, 3 dwts.	18 grs.
Pure Copper	2 "	Pure Silver	5 dwts.
No. 3. 14 Carats Fine.		No. 4. 15 Carats Fine.	
Pure Silver	2½ dwts.	Gold Coin	6 dwts.
Pure Copper	20 grs.	Pure Silver	30 grs.
Pure Zinc	35 "	Pure Copper	20 "
18-carat Gold Plate		Brass	10 "
(formula No. 11)	20 dwts.		
No. 5. 16 Carats Fine.		No. 6. 16 Carats Fine.	
Pure Gold	11 dwts.	Pure Gold	11 dwts. 12 grs.
Pure Silver	3 " 6 grs.	Pure Silver	3 "
Pure Copper	2 " 6 "	Pure Copper	1 dwt. 12 "
		Pure Zinc	12 "

\* See page 35.

No. 7. 18 Carats Fine.		No. 8. 20 Carats Fine, for Crown and Bridge-work.	
Gold Coin	30 parts.	American Gold Coin (21.6	
Pure Silver	4 "	carats fine) \$10 piece, 258 grs.	
Pure Copper	1 part.	Spelter Solder	20.64 "
Brass	1 "		

No. 9. 20 Carats Fine, same use as No. 8.

Pure Gold	5 dwts.
Pure Copper	6 grs.
Pure Silver	12 "
Spelter Solder	6 "

No. 10. 20 Carats Fine, for Crown- and Bridge-work.

Zinc	1½ grs.
Pure Gold	20 "
Silver Solder	3 "

No. 11. Dr. C. M. Richmond's Solder for Bridge-work.

Gold Coin	5 dwts.
Fine Brass Wire	1 dwt.

No. 12. Dr. Low's Formula for Solder in Crown- and Bridge-work.  
19 Carats Fine.

Coin Gold	1 dwt.
Copper	2 grs.
Silver	4 "

Dr. W. H. Dorrance prepares an alloy of

Pure Silver	1 dwt.
Pure Zinc	2 dwts.
Pure Copper	3 "

With this alloy he forms the different grades of gold solders. To form a solder suitable for bridge-work, of 20 carats fine, he melts 4 grains of the alloy with 20 grains of pure gold.

Spelter solder, composed of equal parts copper and zinc, is sometimes employed as a constituent in the preparation of gold solders for the purpose of reducing

the fusing-point. Thus, some dentists use an alloy composed of

18-Carat Gold	6 dwts.
Granulated Spelter Solder	6 grs.

An alloy of this composition is exceedingly brittle, and hence difficult to roll into plate without breaking into many pieces. Its color is good, but the author has noticed that the surface of such solders, after flowing, is apt to be pitted with small holes, and has not the solid and uniform appearance that is desirable. This may be due to the oxidation and escape of some of the zinc.

*Methods of Reducing Gold to a Lower or Higher Standard of Fineness, and of Determining the Carat of any given Alloy.*—The gold alloys used in the laboratory are generally made from pure gold or gold coin, the standards of which are definitely fixed. A few simple rules are here given,\* by which the operator may readily determine the quantity of alloy necessary to reduce either coin or pure gold to any desired standard.

To ascertain the carat of any given alloy, multiply 24 by the weight of gold in the alloyed mass, and divide the product by the weight of the mass. The quotient is the carat sought. For example, take the following :

Pure Gold	18 parts.
Copper	4 “
Silver	2 “
	—
	24 “

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\* Richardson's Mechanical Dentistry.

The result may be thus expressed :

$$24 \times 18 \div 24 = 18 \text{ carats.}$$

To reduce gold to a required carat, multiply the weight of gold used by 24, and divide the product by the required carat. The quotient is the weight of the mass when reduced, from which subtract the weight of the gold used, and the remainder is the weight of the alloy to be added.

To raise gold from a lower to a higher carat, multiply the weight of the alloyed gold used by the number representing the proportion of alloy in the given carat ; divide the product by the figures representing the quantity of alloy in the required carat. The quotient is the weight of the mass when reduced to the required carat by adding fine gold. Thus, to raise one pennyweight of 16-carat gold to 18 carats, the numbers representing the proportions of alloys are obtained by subtracting 18 and 16 from 24. The statement is—

$$6 : 8 :: 1 : 1\frac{1}{3};$$

from which it will be seen that, to raise one pennyweight of 16-carat gold to 18 carats, one-third of a pennyweight of pure gold must be added to it.

Again, if instead of using pure gold we desire to raise the fineness of one pennyweight of 16-carat gold to that of 18, by the addition of, say 22-carat gold, the numbers representing the proportions of the alloy would be found by subtracting, in the example given, 16 and 18 from 22, the result being—

$$4 : 6 :: 1 : 1\frac{1}{2}.$$

Hence each pennyweight of 16-carat gold would re-

quire a half-pennyweight of 22-carat gold to raise it to 18 carats.

The fineness of gold may be expressed in decimals or in parts called carats. The former is the system employed at the United States Mint and by metallurgists and chemists, while the latter is the usual method of expressing the grade of alloys of gold among dentists and jewelers. The following table will show the relation of one to the other :

	Carats.	Decimals.
Pure gold	24	1000
English coin	22	916.6
American coin	21.6	900
Dentists' gold	20	833.3
"    "	19.2	800
Jewelers' gold, best .	18	750
"    " good	15	625
"    " low grade	12	500
Common jewelers' solder	8	333.3

There are many different alloys used in the arts. The greenish alloy used by jewelers contains 70 per cent. of silver and 30 per cent. of gold. "Blue gold" is stated to contain 75 per cent. of iron. The Japanese employ a compound of gold and silver, the standard of which varies from 350 to 500. This alloy is exposed to the action of a mixture of plum-juice, vinegar, and sulfate of copper. They also possess a number of bronzes, in which tin and zinc are replaced by gold and silver. The alloy known as shiya-ku-do, extensively used for sword ornaments, contains 70 per cent. of copper and 30 per cent. of gold.

*Alloys of Gold and Silver.*—The density of those natural alloys, the composition of which varies from  $AuAg_6$  to  $Au_6Ag$ , is greater than that calculated from the densities of the constituent metals. Gold and silver unite in all proportions, affording alloys of several tints, ranging from the color of silver to that of gold. By the addition of silver the hardness of gold is increased, and it is rendered more fusible, while its malleability is not materially diminished. Gold as found in nature always contains silver, and all specimens of native silver will likewise be found to contain gold.

*Gold and Platinum.*—Equal weights of the two metals yield an alloy of good malleability, with, however, some dullness of color. An excess of platinum renders the alloy infusible in an ordinary blast-furnace. One part of platinum to 9.5 of gold will afford an alloy of the same density as platinum.

*Gold and Tin.*—Alloys of tin and gold are hard and brittle, and the combination is attended with contraction. Thus, the alloy  $SnAu$  has a density 14.243, instead of 14.828, as indicated by calculation.

*Gold and Mercury.*—These combine at all temperatures, but the union may be greatly facilitated by heating, and a state of fine division still further assists the process. It is stated that an amalgam composed of six parts of mercury to one of gold crystallizes in four-sided prisms, and that, if the mercury is then distilled off, the gold is left in an arborescent state. The operation of coating the surface of brass or copper objects with gold, extensively practiced some years ago, and known as "fire-gilding," was based upon the amalgamation of gold and mercury. The process is as follows: The article to be gilded is given a uni-

form coating of an amalgam made by heating six parts of mercury with one part of gold, with the surplus mercury removed by squeezing. The operation is greatly facilitated by first rubbing the surface with mercurous nitrate. It is thus given a superficial layer of mercury. It is now gently heated over some burning charcoal, the amalgam in the mean time being kept uniformly distributed over the surface by means of a soft brush. As the heat is continued and the mercury is gradually driven off, the surface assumes a dull yellow color. It is then ready for polishing, which is accomplished by means of a wheel-brush moistened with vinegar. Verdigris mixed with beeswax is applied, for the purpose of removing any remaining mercury by means of the affinity which the latter has for the acetate of copper. This operation, sometimes called "water-gilding," is so dangerous to health, in consequence of the liability of the operator to inhale the volatilized mercury, that it has been almost entirely superseded by electro-gilding.

*Gold and Copper* yield a class of alloys of a reddish color (between gold and copper), which are much harder than either of their constituents. The malleability of the gold is not, however, much affected by admixture of copper, provided the latter is pure. It is stated that seven parts of gold with one of copper exhibits the greatest degree of hardness which it is possible to obtain by union of these two metals. In the American coinage the alloy is chiefly copper; hence the coins are red in color and very hard.

*Gold and Palladium.*—These metals are stated to alloy in all proportions. Chenevix states that an alloy composed of equal parts of the two metals is gray in

color, less ductile than its constituents, and has the specific gravity of 11.08. W. Chandler Roberts, assayer of the Royal Mint, London, states that an alloy of four parts of gold and one of palladium is white, hard, and ductile. According to Makins, the merest trace of palladium with gold will render the latter very brittle. Graham has shown that a wire of palladium alloyed with from twenty-four to twenty-five parts of gold does not exhibit the remarkable retraction which, in pure palladium, attends its loss of occluded hydrogen.

*Gold and Zinc.*—It appears that these two metals possess a strong affinity for each other, but all the alloys of zinc and gold are more or less brittle, according to the quantity of zinc present. Care should, therefore, be observed in the dental laboratory, where so much zinc is employed, that small particles of it do not find their way into the gold filings.

There are certain other metals which, when mixed with gold in quantities as small as the  $\frac{1}{1920}$  part of the mass, render it quite brittle and unworkable. These are bismuth, lead, antimony, and arsenic.

*Compounds of Gold.*—Two compounds of gold with oxygen have been obtained,— $\text{Au}_2\text{O}$  and  $\text{Au}_2\text{O}_3$ ,—but neither of them is of any great practical importance. The chlorids of gold correspond in composition to the oxids.

Auric chlorid, or trichlorid, as it is more commonly called, is prepared by dissolving gold in nitro-hydrochloric acid. The excess of acid is driven off by evaporation at a temperature not greater than  $280^\circ \text{F}$ . ( $=138^\circ \text{C}$ .); otherwise a part of it at least will be converted into aurous chlorid. The crystals obtained



by this process are ruby-red in color, and very deliquescent. The composition of auric chlorid is  $\text{AuCl}_3$ ; atomic weight, 303.1.

Aurous chlorid is obtained by heating the crystallized auric chlorid in a porcelain evaporating-dish to about  $347^\circ \text{F.}$  ( $=175^\circ \text{C.}$ ). If the temperature is carried much beyond this point; say to  $392^\circ \text{F.}$  ( $=200^\circ \text{C.}$ ), the compound will be decomposed into metallic gold and chlorin gas. Aurous chlorid is yellowish in color and nearly insoluble in cold water. Boiling water, however, converts it into auric chlorid and metallic gold. Its composition is  $\text{AuCl}$ ; atomic weight, 232.1.

Auric chlorid is the most important of the compounds of gold, and is the source from which most of the preparations of gold used in the arts are obtained. There are iodids of gold resembling the chlorids in many respects. Berzelius also described an aurous sulfid. These are, however, not important.

Purple of Cassius, named for the discoverer, M. Cassius, is employed by manufacturers of porcelain teeth in obtaining the gum color, and in the industrial arts for imparting a red color to glass and porcelain. It is a compound of gold, tin, and oxygen, which are believed to be grouped according to the formula—



It may be prepared in the humid way by adding stannous chlorid ( $\text{SnCl}_2$ ) to a mixture of stannic chlorid ( $\text{SnCl}_4$ ) and trichlorid of gold. Seven parts of gold are dissolved in aqua regia and mixed with two parts of tin, also dissolved in aqua regia. This solution is

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\* Bloxam's Chemistry, Organic and Inorganic.

largely diluted with water, and a weak solution of one part of tin in hydrochloric acid is added, drop by drop, until a fine purple color is produced. The purple of Cassius, in a state of fine division, remains for a time suspended in the water, but finally subsides as a purple powder. The fresh precipitate dissolves in ammonia, and exposure to light decomposes the purple solution, during which process its hue changes to blue, and it finally becomes colorless, and metallic gold is precipitated, the binoxid of tin being left in solution.

The dry method\* is the one now employed by manufacturers of porcelain teeth in the preparation of gum-enamel. Two hundred and forty grains of pure silver, twenty-four grains of pure gold, and seventeen and a half grains of pure tin are placed in a crucible, with sufficient borax to cover the mass, and melted. In order to insure a thorough mixture of the different metals, the melted mass should be poured from a height into a vessel of cold water, and this process of granulation should be repeated at least three times, but at every melting the alloy should be well covered with borax to prevent loss of the tin by oxidation. The vessel into which the melted mass is poured should not be a metallic one.

The component parts of the alloy having now been thoroughly incorporated, the next step is to collect the granulated mass and separate from it any adherent particles of glass of borax. The metal is then put

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The dry method of preparing purple of Cassius and the process of manufacturing the gum-enamel were imparted to the author by the late Professor Wildman, to whom is due the credit of having brought the preparation of bodies and enamels to their present high state of excellence.

into a glass or porcelain evaporating-dish (the Berlin porcelain is the best), and sufficient chemically pure nitric acid is added to cover the metal. The dish is now placed over a sand-bath, and gentle heat applied and continued until chemical action ceases. If at this point it is found that all the metallic particles are dissolved, the dish may be removed from the bath. Should any solid particles be found in the solution, a little more nitric acid must be added, and the operation continued until all are dissolved. The silver having been entirely dissolved by the nitric acid, the solution should be poured off, and the remaining oxid carefully washed until the last trace of silver is removed. After several washings with a large quantity of pure warm water, the latter should finally be tested with a clear solution of common salt, and if it remains clear, without show of milkiness, the silver is all removed. When the oxid is sufficiently washed, the purple of Cassius should be dried by gently heating, after which it is ready to be incorporated with the silicious materials.

The process of making gum-enamel is divided into three stages : first, the preparation of the oxid ; second, fritting, or by the aid of heat uniting the metallic oxid with the silicious base ; and, third, diluting the frit so as to form the desired shade. The first we have already described. The frit is formed by mixing eight grains of the metallic oxid (purple of Cassius) with seven hundred grains of feldspar, and one hundred and seventy-five grains of a flux composed of—

Pure quartz	4 ounces ;
Glass of borax	1 ounce ;
Sal tartar	1 ounce ;

fused into a glass and ground fine. The oxid is placed in a smooth Wedgwood mortar and ground separately as fine as it is possible to get it. The flux is then added in small quantities, and the levigation continued, after which the feldspar may be added and treated similarly. It is of the highest importance that the mass be reduced to the utmost degree of fineness, and an expert workman will spend six or eight hours at least in levigating the quantity given in the formula. While the mass is being ground in the mortar, foreign substances, such as small particles of wood, etc., must be carefully excluded; otherwise, during the vitrifying process, these will be converted into carbon, which will be sure to reduce a portion of the gold in fine metallic globules distributed throughout the mass.

The vitrifying or fritting process consists in packing the mass, after the most thorough levigation, in the whitest sand crucible that can be obtained. (Dark-colored crucibles are liable to injure the frit by contamination with iron.) This must be provided with an accurately fitting cover made of the same material, or a suitable top may be formed of a piece of slide such as is used in burning continuous-gum work. Before placing the frit in the crucible, the interior surface of the latter should receive a thin coating of very fine quartz, made into a paste with water, to prevent the frit from adhering to it during fusion. The frit in a dry state is then packed in, and the cover tightly luted to its place with kaolin. The crucible is then to be buried in a strong anthracite coal fire, and to remain there until the contents are fused. The time required to do this will depend upon the size of the crucible

and the intensity of the heat. Any ordinary coal-stove provided with a good draught will answer ; but the fuel must be packed around and over the crucible, and the heat carried to the highest attainable point. Usually about two hours will be required to thoroughly fuse the mass, after which it is removed from the fire and permitted to cool.

The vitrified mass is removed from the crucible by breaking the latter. Every particle of adhering quartz or portions of the crucible should be cleared from the surface. It is then pulverized to a fineness which will allow it to pass through a No. 10 bolting-cloth sieve, and is ready for the third stage in the preparation of gum-enamel, which consists of diluting the frit with the proper amount of feldspar. As the strength of the coloring-pigment varies according to the degree of fineness attained during the levigation, it is usually necessary to make several tests in order to arrive at the desired shade. This is accomplished by mixing separately several different lots in the following proportions :

Gum frit	1 part ;
Feldspar	2 parts.
Gum frit	1 part ;
Feldspar	3 parts.
Gum frit	1 part ;
Feldspar	4 parts.

These are applied to marked pieces of porcelain body and fused in the usual way, the result determining the proportions necessary to produce the desired shade.

There is a compound known as "silicate of gold," used in ceramic dentistry to impart a life-like yellow tint to porcelain teeth. This is prepared by grinding

together in a Wedgwood mortar one hundred and twenty grains of coarse feldspar, ten grains of gold foil, and eight grains of flux.\* These are ground until the gold is entirely cut up, when the mass is made into a ball and placed on a slide and fused, after which it is again ground fine and is then ready for use.

Hyposulfite of gold and soda, the *sel d'or* of the photographers, is a double salt formed by adding a solution of one part of trichlorid of gold to a solution of three parts of hyposulfite of soda. Alcohol, in which the double salt is soluble, is then added. The formation of this compound may be explained by the equation,  $8(\text{NO}_2\text{S}_2\text{O}_3) + 2\text{AuCl}_3 = \text{Au}_2\text{S}_2\text{O}_3, 3(\text{Na}_2\text{S}_2\text{O}_3) + 6\text{NaCl} + 2(\text{Na}_2\text{S}_4\text{O}_6)$ .

*Fulminating Gold.*—When ammonia is added to trichlorid of gold, a buff-colored precipitate results, which explodes violently when gently heated. Its exact composition is not well established.

*Discrimination of Gold.*—Protochlorid of tin is a characteristic test for gold, affording a purple-brown precipitate. The smallest portion of gold dissolved in a large quantity of water may be detected by the addition of a few drops of this reagent. Thus, a pale brown precipitate may be obtained in a pint of water containing but one-fiftieth of a grain of gold.

Ferrous sulfate is also a delicate test for the presence

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\* White bottle-glass, which does not contain lead or iron, may be used to reduce the fusing-point of enamels, but, owing to the uncertainty of the composition of glass, most of the manufacturers of porcelain teeth make a fine glass, for this purpose, of the following proportions: Pure quartz, four ounces; glass of borax, one ounce; sal tartar, one ounce. These are first ground separately, then thoroughly mixed, and placed in a white crucible provided with a cover, which must be tightly luted, and then thoroughly fused in the fire. If perfectly pure materials are used the result will be an exceedingly brilliant, colorless, and transparent glass.

of gold, and will detect the merest trace of it. By this reagent the gold is thrown down in the form of a brown powder, which, after washing, drying, and heating to redness, yields the metal in a finely divided state.

Sulfuretted hydrogen ( $H_2S$ ) added to a solution of trichlorid of gold affords a brown precipitate of auric sulfid. Nitrate of mercury also precipitates from solution a brown powder, which after heating yields finely divided gold. Finely divided gold, suspended in water, imparts a violet or red color to it. Colored fluids containing minute particles of gold in a state of suspension may be obtained by the action of phosphorus dissolved in ether upon a very weak solution of gold in aqua regia. After standing for a long time the fine particles of gold are deposited, having the same tint as that which they previously exhibited when suspended in the liquid. The blue particles, being less minute, are soonest deposited, but the red particles require many months to settle down. The one-hundredth of a grain of gold is capable of imparting a deep rose-color to a cubic inch of fluid, and the different colors thus produced are taken advantage of in painting upon porcelain, a beautiful ruby-red color being the result of the pigment thus obtained.

*Assays of Gold Ores, Quartz, etc.*—The specimens of ores should first be heated to redness, and then thrown into cold water to facilitate powdering, which may be accomplished in an ordinary Wedgwood mortar. Several lots of three hundred grains each should be weighed and examined separately, and the assays made from these averaged for the result. To the separate portions of powdered ore equal weights

of litharge, half their weights of sodic carbonate, and about half of powdered charcoal, are added and thoroughly mixed with the ore. Each portion is then placed in a crucible, a little borax sprinkled over the top, and it is ready for heating in a suitable blast- or wind-furnace. The heat at first should be gradual, so that the active effervescence caused by the escape of carbonic acid from the soda salt may not force portions of the mixture from the crucible. After a short time, however, the danger from this cause having passed, the heat may be carried to bright redness, or until the whole has fused. An ingot-mold with two apertures has been recommended for the reception of the fused mixture, which at this point is ready for pouring, the slag being turned into one concavity and the reduced metal into the other. The button will be found to consist of lead and gold, the former reduced from the litharge and the latter from the auriferous ore. These are to be separated by cupellation.

If the ore contains much iron pyrites, or is of the nature of "sweep" (the name given to residues which accumulate in the dental laboratory and other places where gold is worked), it will be necessary to roast it in a shallow fire-clay dish placed in a muffle; and, in the case of pyrites containing about seven penny-weights to the ton, the operation should be conducted with one thousand grains. The roasted ore is then fused with a mixture consisting of red lead, one thousand grains; sodic carbonate, six hundred grains; powdered charcoal, forty grains, and borax, five hundred grains. The mixture is introduced into a clay crucible, which it should half fill, and is fused in an air-furnace. The button of reduced lead may be



removed either by pouring the contents of the crucible into a mold, or by breaking the crucible when cold.

*Assay by Scorification.*—Scorification resembles cupellation,\* but the oxid of lead produced in the operation, instead of sinking into a porous cup, is held in a flat saucer of fire-clay, and dissolves the earthy constituents of the ore, leaving the precious metal to pass into another portion of lead, which remains in the metallic state. About two hundred grains of the roasted ore are placed in the scorifier, and intimately mixed with five hundred grains of granulated and fifty grains of borax lead. The contents of the scorifier are fused in a muffle. Air is admitted to oxidize the greater portion of the lead. At the conclusion of the operation the litharge should be perfectly fluid and cover the molten lead. The slag may be freed from particles of precious metal by the addition, at the conclusion of the operation, of a small quantity of powdered anthracite, which reduces a portion of the litharge to metallic globules, which fall through the slag and unite with the lead button. The gold is then separated by cupellation, and the silver, with which it is almost always associated, by parting with nitric acid.

*Assaying.*—This term refers to the quantitative estimation of one constituent of an alloy or mineral, and is accomplished by cupellation when the alloying metal is copper, and “parting” when the debasing metal consists of silver. Usually both operations are necessary. From five to sixteen grains of the gold are wrapped in sheet lead, with pure silver equal to two and a half times the quantity of gold supposed

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\* See page 158.

to be present. The weight of lead employed where the assay is standard gold\* is 8 to 1, and the ratio of the weight of lead to the weight of copper assumed to be present is 100.1. The assay is now to be treated by cupellation, a process which is thus briefly and clearly described by Mr. W. Crookes :

“ The gold alloy is fused with a quantity of lead and a little silver, if silver is already present. The resulting alloy, which is called the ‘lead button,’ is then submitted to fusion on a very porous support, made of bone-ash and called a ‘cupel.’ The fusion is effected in a current of air, which oxidizes the lead. The heat is sufficient to keep the oxid of lead fused. The porous cupel has the property of absorbing melted oxid of lead without taking up any of the metallic globules, exactly in the same way that blotting-paper will absorb water while it will not touch a globule of mercury. The heat being continued, and the current of air† always passing over the surface of the melted lead button, and the oxid of lead or litharge being sucked up by the cupel as fast as it is formed, the metallic globule rapidly diminishes in size until at last all the lead has been got rid of. Now, if this were the only action, little good would have been gained, for we should have put lead into the gold alloy and taken it out again. But another action goes on while the lead is oxidizing in the current of air. Other metals, except the silver and gold, also oxidize, and

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\* 22-carat, or coin.

† The process of cupellation is generally performed in a furnace provided with a muffle for the reception of the cupels, and arranged so as to admit of a current of air over the fused button. The lead used in cupellation should be of absolute purity; otherwise, as lead is always liable to contain silver, the latter would necessarily combine with the assay and vitiate the accuracy of the result.

are carried by the melted litharge into the cupel. If the lead is, therefore, rightly proportioned to the standard of alloy, the resulting button will consist of only gold and silver, and these are separated by the operation of parting, which consists in boiling the alloy (after rolling it into a thin plate) in strong nitric acid, which dissolves the silver and leaves the gold as a coherent sponge."\*

As the accuracy of the result of an assay is liable to be influenced, either by retention of silver or copper, or by loss of gold by volatilization in the muffle, solution in the acid, or retention in the cupel, it is necessary to employ "check assays," made on pure gold, with which the alloy assay is weighed in comparison; and, as will be seen, the weight of gold indicated by the balance is liable to be either greater or less than the quantity originally present in the alloy. The following formula† will serve to show the correction to be applied:

Let 1000 be the weight of alloy originally taken.

$p$ , the weight of the piece of gold finally obtained.

$x$ , the actual amount of gold in the alloy expressed in thousandths.

$a$ , the weight of gold (supposed to be absolutely pure) taken as a check, which approximately equals  $x$ .

$b$ , the loss or gain of weight experienced by  $a$  during the process of assay, expressed in thousandths.

$k$ , the variation of "check gold" from absolute purity, expressed in thousandths.

Then the actual amount of fine gold in the check-piece  $= a(1 - \frac{k}{1000})$ , and  $x$ , the corrected weight of the assay, will  $= p - \frac{ak}{1000} + b$ ;  $b$  being added or subtracted according as it is a loss or gain.

\* See "Quartation."

† Annual Report, Mint of England.

If  $a$  be assumed to be equal to  $x$ , this equation becomes

$$x = \frac{p + b}{1 + \frac{k}{1000}}$$

*Example.*—Let  $p = 901.1$  thousandths

$$a = 920.0 \quad "$$

$$b = 0.3 \quad " \quad \text{gain in weight.}$$

$$k = 0.1 \quad "$$

Then by the first formula

$$x = 901.1 - \frac{220 + 0.1}{1000} - 0.3$$

For, as  $b$  is a gain in weight, it must be deducted. Hence,

$$x = 901.1 - 0.092 - 0.3.$$

$$= 900.708.$$

And by the second formula

$$x = \frac{901.1 - 0.3}{1 + \frac{0.1}{1000}} = 900.708.$$

*Gold Leaf and Foil.*—Gold designed for manufacture into leaf is variously alloyed, according to the color required. The following is a list showing the proportions of alloy per ounce required to produce certain tints :

Color of Leaf.	Proportions of Gold.	Proportions of Silver.	Proportions of Copper.
	Grains.	Grains.	Grains.
Red .	456.460	—	20.24
Pale Red .	464.	—	16.
Extra Deep Red	456.	12	12.
Deep Red	444.	24	12.
Citron	440.	30	10.
Yellow	408.	72	—
Pale Yellow	384.	96	—
Lemon .	360.	120	—
Green or Pale .	312.	168	—
White	240.	240	—

For filling teeth nearly pure gold in the form of foil is used. It is generally prepared by beating, but some of the heavier numbers are produced by rolling. There are two varieties, cohesive and non-cohesive, extensively used in the United States at the present time, the methods of manipulating which are widely different. In the former the characteristic quality of cohesiveness, which is greatly diminished by compression of the fibers in beating, is restored by heating to redness, and this is best effected by placing the foil upon a sheet of mica, which is held over a spirit-lamp. The habit common among dentists, of taking up the foil on the point of the plugger and passing it through the flame of a spirit-lamp, is not productive of the best results, the gold being made harsh by contact with the flame, whereas it should, in addition to cohesiveness, possess at least some of the kid-like softness of the non-cohesive variety. Some of the manufacturers of gold foil for dental purposes produce a "soft" variety, in which cohesiveness cannot be developed by heating. This quality may be attained by alloying, or by depositing carbon upon the surface, as the latter cannot be driven off by heating.

The statement has been made by one of the most experienced manufacturers of dental foils in this country, that he makes the two varieties of cohesive and non-cohesive foils from the same ingot. As his non-cohesive or "soft" foil is unsurpassed in the qualities which are desirable for such a foil, it seems proper to assume therefore that the development of these qualities is due either to some treatment of the surface or to mechanical management during lamination, and not to alloying.

The manufacture of non-cohesive gold foil properly so called is not, it would seem, understood by every gold-beater. Some of them prepare only cohesive foil, while others offer for sale a so-called non-cohesive foil, which is really nothing more than an unannealed sample of the cohesive type, and which is destitute of the peculiar "kid-like softness" and toughness which permits it to be carried forward by the plugging instrument into deep cavities without fracture. The extent to which the characteristic qualities of cohesiveness, etc., may be modified or entirely lost by the absorption of gases has yet to be fully studied. In 1866 Graham demonstrated that gold is capable of occluding 0.48 of its volume of hydrogen, and 0.20 of its volume of nitrogen. Varrentrapp has also pointed out that "cornets" from the assay of gold may retain gas if they are not strongly heated.

Prof. G. V. Black deserves credit for his researches published in the *Dental Cosmos*, vol. xviii, p. 138, showing the influence of gases and moisture on the cohesiveness of gold foil.

The corrugated gold introduced about fifteen years ago belongs to this class of foils. It is prepared by placing the sheets of gold between leaves of a particular kind of unsized paper, and tightly packing it in iron boxes, which are exposed to a temperature sufficiently high to carbonize the paper. These are then allowed to cool, and on opening them the gold is found to be exceedingly soft and non-cohesive, and to present a peculiar corrugated condition of surface, while it is incapable of being rendered cohesive by annealing.

Non-cohesive foil is used in the form of cylinders, made by rolling a ribbon or strip of foil, or as pellets,

mats, or ropes. These are introduced into the cavity by means of plugging instruments with or without serrations, the force employed being for the most part hand-pressure, though the hand-mallet is much used by many operators as a means of impacting non-cohesive foil. The advantages claimed for non-cohesive foil are that less time is consumed in its introduction, and that in consequence of the greater softness which it possesses it is capable of being more thoroughly burnished to the edges of the cavity.

When non-cohesive foil is used, union does not take place between the particles of gold introduced into the cavity. They are simply made to adhere mechanically by wedging the mats, cylinders, or pellets, as the case may be, one against the other, into a cavity properly prepared to retain them. On the other hand, between particles of gold wherein the characteristic quality of cohesiveness remains unimpaired, that property manifests itself whenever two pieces are brought in contact, and if cohesion be facilitated by the application of sufficient force, homogeneity results. Hence, the methods of operating with the two kinds of foil must necessarily differ. Non-cohesive foil is introduced in pieces of more or less bulk ; the cohesive variety is introduced in much smaller proportions, each piece being carefully welded to the others by means of the electro-magnetic mallet, the hand-mallet, the "automatic" plugger, or by hand-pressure.

The method of preparing cohesive foil is thus described by the late Dr. M. H. Webb, of Lancaster, Pa. : "A half-leaf of No. 4 gold foil for small, a whole sheet for medium, and two leaves for large fillings, should be taken from the book by means of the foil-carrier or

spatula, and placed upon a piece of spunk covered with white kid. The foil should be folded with an ivory spatula into a tape-like form, eight or ten lines in width respectively, which is then cut across into small pieces about one-twelfth of an inch in width. Heavy foils, ranging from No. 30 to No. 60, may be advantageously employed in extensive contour operations. The ordinary light numbers, however, when prepared in the manner described, can more easily be impacted into small cavities, fissures, and grooves."

For cohesive gold the cavity is carefully prepared, the edges of enamel being smoothly and evenly finished. A groove or undercut is then made toward the cutting-edge and toward the cervical wall, and a starting-point drilled in the dentine toward the palatal edge for the purpose of anchorage. Into this the gold is carried by means of hand-pressure, and by the same means worked into the grooves or undercuts. The point in which to start the filling should be only sufficiently deep to retain the small pieces of gold first introduced while others are being built upon them. When the first pieces are firmly fixed, the electromagnetic mallet may be employed to the end. If the cavity be small, the gold should be prepared from a half-leaf of No. 4 foil, so folded as to be equivalent to No. 12 or No. 16, and then cut into strips about one-twenty-fourth of an inch in width.

Although much diversity of opinion exists among dentists regarding the relative value of cohesive and non-cohesive foils, it may with safety be stated that, skillfully directed, either is capable of affording good results. But, like all other filling-materials, each has its proper place. Thus, in a majority of crown-cavi-



ties, it would be a sheer waste of time to fill exclusively with cohesive foil; while, on the other hand, there are many approximal cavities in which the walls have been rendered so thin by the progress of decay that probably the electro-magnetic mallet alone could be relied on to thoroughly impact the gold to walls and periphery. In such cases the cohesive foil should be folded of No. 4, and cut into narrow strips as above described, the main object being to avoid the application of much force, such as would be required in the consolidation of large mats or cylinders of non-cohesive gold. Indeed, it may be stated that one of the greatest advantages in filling with cohesive foil by the electro-magnetic mallet is the thoroughness and safety with which the gold may be packed against very frail walls.

The merits of the cohesive and non-cohesive forms of foil are by their respective advocates often unfairly presented, but the value of each may be stated as follows: Cohesive foil in very small pieces is, with the electric plugger, capable of being brought into perfect apposition with the most delicate walls of enamel with comparatively little danger of fracture; non-cohesive foil, in much larger masses, may with less expenditure of time be introduced into cavities where the walls are sufficiently strong to withstand the force required to consolidate the mats or cylinders, and, so far as the preservation of the tooth is concerned, affords equally good results.

*Gold-Beating.*—In all probability the art of gold-beating originated among Oriental communities, with whom the love of gold ornaments has always been a distinguishing characteristic. The art is of great

antiquity, and is referred to by Homer and Pliny. On the coffins of Theban mummies specimens of leaf-gilding were met with, where the gold in a very thin state resembled modern gilding. It is stated that the Incas of Peru did not understand the art of gold-beating beyond the preparation of sheets or plates, which they nailed on the walls of their temples.

The process of beating gold is conducted in the following manner: The metal is first alloyed according to the color desired, and, in order to improve its malleability, it is melted at a higher temperature than is necessary for mere fusion. It is then cast into an ingot and rolled into a ribbon of a half-inch in width and ten feet in length to the ounce. After this it is annealed and cut into pieces of about six and a half grains each, and placed between the leaves of a "cutch," which is about half an inch thick and three and a half inches square, containing about one hundred and eighty leaves of a tough paper manufactured in France. Fine vellum was formerly much used for this purpose, and it is yet often interleaved in the proportion of about one of vellum to six of paper. The hammer employed by gold-beaters weighs about seventeen pounds, and rebounds, by the elasticity of the skin, to such an extent that each stroke involves but little labor. It requires about twenty minutes' beating to spread the gold to the size of the cutch, and if it is intended for filling teeth it is carried no further than the cutch stage. If, however, it is to be still further attenuated, each leaf is taken from the cutch and cut into four pieces, when it is put between the skins of a "shoder," four and a half inches square and three-quarters of an inch thick, containing about

seven hundred and twenty skins. The shoder requires about two hours' beating with a nine-pound hammer. As the gold will spread unequally, the shoder is beaten upon after the larger leaves have reached the edges, the effect of which is that the margins of larger leaves come out of the edges in a state of dust. This allows time for the smaller leaves to reach the full size of the shoder, by which a general evenness in the size of the leaves is obtained. Each leaf is again cut into four pieces and placed between the leaves of a "mold,"—an appliance composed of about nine hundred and fifty of the finest gold-beaters' skins. Its dimensions are five inches square by three-fourths of an inch thick. The management of the gold in the "mold" is the last and most difficult stage in the process of gold-beating, and the fineness of the skin and judgment of the workman will greatly influence the final result.

The process of lamination may be thus described : During the first hour the blows of the hammer are directed principally upon the center of the mold, by which means the edges of the leaves are made to crack, but they soon coalesce and unite ; so that, after beating, no trace of the rupture is left. After having been beaten for an hour in a mold, until the leaves have attained a thinness of  $\frac{1}{150000}$  part of an inch in thickness, green rays of light begin to be transmitted, if the gold be pure ; but, if largely alloyed with silver, rays of a pale-violet hue pass through the gold.

The membrane called "gold-beaters' skin," used in the make-up of the shoder and mold, is the outer coat of the cæcum or blind gut of the ox. It is immersed in a potash solution, and scraped with a blunt

knife to free it from fat. It is then stretched on a frame, two membranes are glued together, treated with camphor in isinglass, and subsequently coated with albumen, and cut into squares of five or five and a half inches, and is ready for use. It is stated that the cæca of three hundred and eighty oxen are required to yield enough of the membrane to make up one mold of nine hundred and fifty pieces, only two and one-half skins being obtained from each animal. Dryness is a matter of great importance, and, as the leaves are liable to absorb moisture from the atmosphere, they require hot-pressing every time they are used, and if this precaution is neglected the leaf will be pierced with innumerable holes or reduced to a pulverulent state.

## CHAPTER IX.

### SILVER.

ATOMIC WEIGHT, 108. SYMBOL, AG (ARGENTUM).

SILVER may be classed as next to gold in its manifold uses and great malleability and ductility. It has been known from the earliest ages, and, alloyed with certain proportions of copper, it has been adopted by all civilized nations for purposes of coinage, and for articles of plate and ornamentation.

*Properties of Silver.*—It is distinguished from all other metals by its brilliant whiteness. Its specific gravity is 10.53. In hardness it is between gold and copper. It is one of the most ductile and malleable of the metals,—indeed, when calculated by weight, it is not even surpassed by gold. For example, one grain of gold may be beaten out to the extent of 75 square inches, and the same weight of silver to 98 square inches. Taking a cubic inch of gold at 4900 grains, this gold leaf is  $\frac{1}{369650}$  part of an inch in thickness, or about 1200 times thinner than ordinary printing-paper.\* But the silver, though spread over a larger surface, will be thicker, owing to the difference of specific gravity between gold and silver. The extent of the malleability of gold and silver has not yet been definitely determined, as the means employed

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\*Gold has, for the sake of experiment, been beaten out to the extent given above, but the  $\frac{1}{300000}$  of an inch, as given on page 119, is as thin as is ever required for practical purposes.

to test it have failed before there was any appearance of the malleability of either of them being exhausted.\*

In tenacity silver surpasses gold. It fuses at about  $1873^{\circ}$  F., and during the fusion absorbs oxygen to the extent of about twenty-two times its own volume; but at the instant of solidification it undergoes considerable expansion, while at the same time it parts with the oxygen, which makes its escape through the thin crust formed over the fluid metal, carrying with it fine globules of the metal, which may be observed adhering to the sides of the crucible. It is the best conductor of heat and electricity known. It possesses no direct attraction for oxygen; hence it is not oxidized by dry or moist air at any temperature. It is, however, oxidized by ozone, and tarnished by air containing sulfuretted hydrogen, which blackens the surface with a superficial layer of sulfid of silver, which may be removed by a solution of cyanid of potassium.

With the exception of nitric, silver is not affected by dilute acids; but hot concentrated sulfuric acid converts it into sulfate of silver, and when boiled with strong hydrochloric acid it dissolves to a slight extent in the form of chlorid of silver, which is precipitated by the addition of water.

*Occurrence and Distribution.*—In the middle ages Austria was the chief source from which silver was obtained, as an associate metal with lead. At the present day the United States, Peru, and Mexico supply large quantities.

Silver is found, first, as native silver, occurring in flat masses occasionally, and sometimes crystalline in form. In this country it occurs with native copper,

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\* W. Chandler Roberts, Assayer Royal Mint.

masses frequently being met with in which the two metals are diffused, the silver showing in specks upon the copper.

Native silver is usually free from any considerable admixture with other metals, although it invariably contains traces of gold, antimony, etc. It is also found as chlorid, iodid, and bromid.

The most common ores from which silver is derived are those resulting from combination with sulfur as sulfids. These may be divided into three kinds: First may be mentioned the common sulfid, of Mexico, called vitreous sulfid. It is a protosulfid, is very fusible, and readily yields silver when made to give up its sulfur. Another sulfid, closely resembling the first, called brittle silver ore, is found in South America and in some parts of Europe. It is readily decomposed by heat, and, during exposure to high temperatures, evolves fumes of arsenic and antimony. A third sulfid, found in nearly all silver mines in the form of ruby-colored, transparent crystals, is called red silver ore, and is associated, to some extent, with oxids. The composition of this ore has been given as follows: Silver, 56 to 62; antimony, 16 to 23; sulfur, 11 to 14; oxygen, 8 to 10.

The chlorid or native horn-silver is quite an abundant ore of South America (Chili). It is a true chlorid, and, like precipitated chlorid of silver, darkens when exposed to sunlight. Its composition is given as, silver, 75.3; chlorin, 24.7.

*Methods of Separating Silver from its Ores.*—As much of the silver of commerce is extracted from ores too poor to admit of its economical separation by any process of melting or fusing, even in regions where

fuel is plenty, recourse to the method known as "amalgamation" is necessary. This depends simply upon the easy solubility of silver and associated metals in mercury. The ore is crushed to powder, mixed with a sufficient quantity of common salt, and roasted at a dull-red heat in a suitable furnace. By this treatment any sulfid of silver contained is converted into chlorid. The mixture, which consists of much earthy matter, metallic oxids, soluble salts, silver chlorid, and metallic silver, is sifted and placed in barrels arranged to revolve on axes. Scraps of iron and water are added, and the whole agitated together for the purpose of reducing the silver chlorid to the metallic state. A sufficient quantity of mercury is then added, and the agitation continued until the metallic particles are dissolved, forming a fluid amalgam which is readily separated from the mud or earthy matter by subsidence and washing. It is then strained through a strong linen cloth or other suitable fabric to separate the fluid mercury from the more solid portions of amalgam. These latter are subsequently exposed to heat in a retort, by which the remaining mercury is distilled off. The silver, more or less impure from admixture with other metals contained in the ore, is thus obtained.

In order to prevent loss during the amalgamation process, in consequence of a tendency on the part of the mercury to combine with sulfur, oxygen, etc., technically known as "flouring," in which condition it may be washed away, together with the silver it has taken up, from one to two per cent. of sodium is added to the mercury. The great affinity of sodium for sulfur and oxygen prevents "flouring" of the mercury.

Considerable quantities of silver are obtained from



argentiferous galena,\* and, indeed, it may be stated that nearly every specimen of native lead sulfid will be found to contain traces of the nobler metal. When the proportion of the precious metal present is sufficiently large to insure its profitable separation, the ore is reduced as usual,† the silver remaining with the lead, and is then treated according to a process discovered by Mr. Pattinson, by whom it was found that, when lead containing a considerable amount of silver is fused and carefully stirred while it is allowed to cool slowly, crystals much less rich in silver than the mass before melting will form, and separate and subside to the bottom. These crystals of poorer lead are removed by means of perforated ladles. The silver is thus concentrated. This method of separating silver from lead, as practiced on a large scale, is thus described by Mr. Makins in his "Manual of Metallurgy :"

"A series of iron pots, from nine to twelve in number, are employed. These are hemispherical, about five feet in diameter, and calculated to hold a charge of about nine tons of metal each. They are set in brick furnaces adjacent to one another, but with quite distinct flues, furnaces, dampers, etc. The lead, assorted according to its richness in silver, is then placed in the pots in the following order : Some lead containing ten ounces of silver per ton having to be worked, nine tons of it would be placed in the fifth pot and melted. After complete fusion it is skimmed with a perforated ladle, which removes the dry oxids for subsequent reduction, while it permits the fluid lead to run

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\*Silver is invariably present in this form of lead ore, but not always in paying quantities.

†See chapter on "Lead."

back into the pot. The fire is then drawn, and the metal stirred while it slowly cools until it begins to thicken. The workman at this stage of the operation employs an iron ladle of eighteen inches in diameter by five inches deep, perforated with half-inch holes, and furnished with a very long handle. This handle he raises above his head, sinking the bowl into the lead until it reaches the bottom. Then, by using the handle as a lever, and depressing it as far as possible, the ladle full of crystals is brought into view, and, by means of a hook and chain fastened to a crane, is suspended and left to thoroughly drain, after which the crystals are turned into the fourth pot. This operation is continued until two-thirds of the lead in the fifth pot has been passed over in crystals to the fourth pot, under which a fire is made and the crystals again melted. The remaining three tons of molten lead in the fifth pot, which by the separation of the crystals contains silver equaling twenty ounces per ton, is now ladled into the sixth pot. The results of the preceding operations may be summed up as follows: In pot 5, nine tons of ten-ounce lead equals ninety ounces of silver, of which six tons of five ounces (thirty ounces silver) works into pot 4; and three tons of twenty ounces (sixty ounces silver) is ladled into pot 6. The work now proceeds until all the pots are in operation. Three tons of five-ounce lead would be added to the six tons passed into pot 4, while six tons of twenty-ounce lead would be carried into pot 6. Six tons from pot 6 would work into number 5, and three tons in bottoms will be put back into the same pot from number 4, filling it again without the addition of pig-lead. The bottoms or portions which remain after the ladling

become by that process so rich in silver as to often contain six hundred ounces to the ton. This is finally submitted to cupellation, by which means the complete separation of the silver is effected."

The cupel and its application may be thus briefly described: Bone-ash is mixed with water, made into a cup, in a suitable mold, and dried. This is called the cupel,\* and has the property of absorbing oxids when they are combined with oxids of lead in a state of fusion. Impure silver is mixed with a certain quantity of lead, determined by the amount of impurity supposed to exist in the alloy. The mixture is melted in the cupel in a current of air until the whole of the lead is converted into oxid, which, in a fused state, sinks into the porous cupel, carrying along with it the other impurities, the silver being left behind in a pure state. The whole operation is based on the absence of attraction for oxygen evinced by the noble metals even when exposed to high temperatures, and on the affinity possessed by the base metals for oxygen under similar conditions.

Cupellation may be accomplished either in a muffle arranged with reference to the passage of a current of air, so that oxygen may be freely supplied to the melted metal, or it may be performed under the oxidizing flame of the blow-pipe. The latter operation is often employed in blow-pipe analysis. A certain amount of the alloy is mixed with about four times its weight of pure lead, and then placed on the cupel and the oxidizing flame of the blow-pipe directed on it. The oxidizing process soon begins, and in about thirty minutes all the lead will be converted into litharge,

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\* These may be obtained at the chemists' furnishing-shops ready for use.

which is fusible, and is readily absorbed into the porous substance of the cupel, carrying with it all the oxidizable metals that may be present. At this point, the button having parted with every trace of the latter, assumes an exceedingly bright appearance, technically called the "brightening of the button," thus offering a certain means of ascertaining when the process of cupellation is complete. Cupellation, under the oxidizing flame of the blow-pipe, for quantitative discrimination, requires careful management, particularly when the silver has parted with the base metals and approaches a state of purity. For it is at this stage of the operation that the well-known property of melted silver, of absorbing oxygen from the atmosphere, and then parting with it as it approaches the point of solidification, may be observed. The giving-off of the absorbed oxygen is what causes "sputtering," by which minute globules of the metal are thrown off and lost, thus rendering the assay inaccurate.

Besides the method of obtaining silver above described, the metal may be obtained by converting sulfids into chlorid, the latter being easily reduced to metallic silver by the wet method. The sulfid is also sometimes converted into sulfate, when the silver may be reduced from the solution by precipitation.

Another method of separating silver from its ores consists in roasting the latter with common salt to convert the silver into chlorid, which is dissolved out of the mass by means of a strong solution of chlorid of sodium; the silver is then recovered in the metallic state by precipitating with copper. Hyposulfite of soda has also been employed to dissolve out the chlo-

rid of silver, the resulting solution being precipitated by sulfid of sodium, yielding sulfid of silver, which requires roasting to drive off the sulfur and liberate the metallic silver.

*Compounds of Silver.*—There are three compounds of silver with oxygen: the suboxid,  $\text{AgO}$ ; the oxid,  $\text{Ag}_2\text{O}$ ; and the peroxid, which is thought to have the formula of  $\text{Ag}_2\text{O}_2$ . The oxid is the only one having any practical importance. Being the base contained in the salts of silver, it is obtained by adding caustic potassa or baryta-water to a solution of nitrate of silver.

Silver nitrate ( $\text{AgNO}_3$ ) is prepared by dissolving silver in nitric acid by the aid of gentle heat, after which it is evaporated to dryness or until it crystallizes. These crystals are colorless, transparent, and soluble in an equal weight of cold and in half the quantity of boiling water. They are also soluble in alcohol. Nitrate of silver is fusible, and when poured into cylindrical molds forms the lunar caustic employed by surgeons. At high temperatures (red heat) it is decomposed, yielding pure metallic silver.

Silver sulfate ( $\text{Ag}_2\text{SO}_4$ ) is prepared by boiling metallic silver in sulfuric acid.

Silver sulfid is remarkable for being so soft and malleable that medals may be struck from it. It may be formed as a black precipitate by the action of hydrogen sulfid ( $\text{H}_2\text{S}$ ) upon a solution of silver nitrate, or it may be formed by heating silver with sulfur in a covered crucible. It is the affinity existing between these two elements which renders the combination of silver and vulcanizable rubbers impracticable. Silver sulfid is not soluble in dilute sulfuric or hydrochloric

acid, but is readily dissolved by nitric acid. Metallic silver also dissolves sulfid of silver when melted with it.

Silver chlorid ( $\text{AgCl}$ ) is the form into which silver is commonly converted in separating it from other metals or from its ores. It is a white, curdy precipitate, and may be obtained from a solution of the nitrate by the addition of sodium chlorid or hydrochloric acid. When freshly prepared it is perfectly white, but soon darkens, and eventually becomes quite black by exposure to solar light, parting with a portion of its chlorin, and becoming a subchlorid ( $\text{Ag}_2\text{Cl}$ ).

Silver chlorid may also be formed by suspending a silver leaf in a glass vessel containing chlorin gas, and when thus prepared it is not blackened by exposure to light. Argentic chlorid is fusible at  $500^\circ\text{F}$ . A much higher heat converts it into vapor, but does not decompose it. It is soluble in ammonia.

*Discrimination.*—The chlorids and hydrochloric acid precipitate white argentic chlorid, and so delicate is the test that when one part of silver is dissolved in 200,000 times its weight of water it may be readily detected by the opalescence which is imparted to the fluid by the precipitant. This precipitate is always changed to a violet-black by exposure to light, but the presence of mercury\* will prevent discoloration. It is insoluble in nitric acid, but is readily soluble in ammonia, and may be fused to a horny mass without decomposition.

Sulfuretted hydrogen added to a solution containing silver throws down a black precipitate of silver sulfid, which is not soluble in dilute acids, alkalies, or potassic cyanid. Sulfuric acid at a temperature of

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\* Mercurous chlorid.

212° F will, however, dissolve it, with separation of the sulfur.

Ammonia or potassa, when employed as a precipitant, throws down a brown oxid, insoluble in the latter, but soluble in the former, and if freely exposed to air this solution will deposit fulminating silver.

The blow-pipe is frequently used in the discrimination of silver compounds, which when heated on charcoal with sodic carbonate yield a bright bead of metallic silver, often accompanied by a red-colored deposit on the charcoal.

Quantitatively, the estimation of silver may be accomplished either by the usual humid process or by assaying. The first consists in precipitating the metal as chlorid, which is to be separated and weighed. The precipitation is effected as follows : The silver solution is acidulated by nitric acid ; hydrochloric acid or sodic chlorid, slightly in excess, is then added ; but, as silver chlorid is to a certain extent soluble in either of these, an undue excess must be avoided. The chlorid must now be carefully and repeatedly washed and filtered in a thoroughly dry filter, previously weighed. After the solution has passed through the filter, the latter with its contents is dried and weighed, and the weight, minus the weight of the filter, will be the quantity of silver chlorid present.

The dry method or assaying process consists in forming an alloy of the silver with lead, and is especially applicable to ores and the sweep of the dentist's laboratory. The specimen to be treated is heated with from twelve to thirty times its weight of pure granulated lead in a bone-ash cupel, which is placed in a muffle so arranged that a current of atmospheric air

may pass freely over the vessel and oxidize the lead. This oxid of lead, being quite fusible, combines with any base metal present and oxidizes it, uniting subsequently with the oxid as a fusible slag, while the gold or silver will be held by the unoxidized portion of the lead. In the treatment of specimens of alloys, such as plate or coin, a quantity of the specimen is accurately weighed and mixed with from four to five times its weight of pure granulated lead. It is then placed in the cupel and exposed to heat, as above described, until all the lead is oxidized or converted into litharge, when the remaining button assumes the brilliant appearance of surface before alluded to, which denotes that the base metals or oxidizable constituents have been oxidized and taken up by the lead oxid. This button is then to be weighed by means of a delicate assay balance, and the loss of weight shows the proportion of alloy that was present.

*Pure Silver.*—Pure silver, which is reckoned as 1000 fine, may be obtained from standard or other grades of silver by dissolving them in nitric acid slightly diluted with water, the solution being much facilitated by exposure to gentle heat. If gold be associated with the alloy it will be found at the bottom of the vessel, in which case it will be necessary to use a syphon to remove the argentic nitrate solution. The silver is now to be precipitated in the form of chlorid by the addition of an excess of common salt. When all has subsided the liquid is carefully poured off, and the chlorid thoroughly washed to remove all traces of acid. The chlorid is then placed in water acidulated with hydrochloric acid (an ounce of chlorid requiring six to eight ounces of water) and pieces of clean



wrought iron put in it, when a copious evolution of hydrogen follows, which, uniting with the chlorine of the argentic chlorid, liberates metallic silver. The latter should not be disturbed until the last particle of it is thus reduced, when it will be found to be a spongy mass. The undissolved iron should now be carefully removed, the ferrous and ferric chlorid carefully decanted, and the silver washed in hot water containing about one-tenth its bulk of hydrochloric acid. This is repeated several times, and finally the silver is again thoroughly washed with pure hot water. The silver, after drying, is then ready for melting, and if care has been observed in the process it will be found to be of a fineness of 999.7 parts in 1000, the 0.3 of impurity present being due to traces of iron. The chlorids may be acidulated with sulfuric acid, and reduced with zinc instead of iron.

Another method of precipitating silver in the metallic form consists in placing a sheet of copper in a solution of argentic nitrate. The metal is thrown down in a crystalline form. Silver thus obtained is never free from traces of copper.

Pure silver can only be obtained from samples of a lower grade by fusing the pure chlorid with sodic carbonate. The reaction is shown in the equation :



Owing to the copious evolution of carbonic acid gas which takes place during the decomposition, some of the silver may be thrown from the crucible, and loss may occur by the absorption by the crucible of some of the fused chlorid. To avoid this the sides of the vessel should be coated with a hot saturated solution of borax.

A composition of 100 parts of argentic chlorid, 70.4 of calcic carbonate (chalk), and 4.2 of charcoal, has been recommended as a means of obtaining pure silver. This mixture is heated to dull redness for thirty minutes, and then raised to full redness; carbonic acid and carbonic oxid are given off; the calcic chlorid is converted into calcic oxychlorid, underneath which, in the bottom of the crucible, will be found the button of pure silver.

*Alloys of Silver.*—In consequence of its softness, silver in the pure state is liable to considerable loss by attrition. For all useful purposes, however, the requisite amount of hardness may be conferred upon it by the addition of a small proportion of copper. Thus, silver for coinage and manufacturing purposes usually contains in 1000 parts from 900 to 925 of silver and from 75 to 100 of copper. The term “standard silver” refers to the metal thus alloyed with copper, that of the United States coinage being silver 900 parts, copper 100.

Previous to the introduction of vulcanized rubber as a base for artificial dentures, standard silver was much employed in the United States for temporary dentures, when cheapness was an important consideration. In England a much more durable alloy is used, in which the alloying metal is platinum, in the proportion of from three to ten grains of the latter to each penny-weight of silver. The advantages possessed by this alloy over ordinary standard silver may be summed up as follows: It resists wear better, and not even a suspicion can be reasonably entertained of any ill effects occurring, either locally or to the general system, from its presence in the mouth. It permits of

the employment of a higher grade of solder, and it is a much more rigid alloy than ordinary standard or coin silver. Hence it makes a stronger artificial denture, which is less likely to have its adaptation impaired by bending. But, while silver is improved in some respects when platinum is the sole alloying component, it must not be supposed that its affinity for sulfur is thus materially lessened, or that its tendency to blacken when brought into contact with that element or its compounds is obviated. Indeed, it may be stated that platinum added to silver in such small quantities does not wholly protect the latter from the action of its ordinary solvents. Such an alloy of silver, for instance, would not only be readily dissolved by nitric acid, but the platinum also, though unaffected ordinarily by that menstruum, would readily yield to it when combined with silver.

This alloy of silver, which is known in England as "dental alloy," often contains from twenty-five to thirty per cent. of platinum. To separate the latter metal from the silver the alloy is dissolved in nitric acid, which on the addition of heat will dissolve all of the silver with about ten per cent. of the platinum. On introducing a bar of copper into this solution, the silver and platinum are quickly precipitated in a metallic state. This precipitate is again placed in nitric acid, which redissolves the silver, leaving the platinum untouched, which, however, may be dissolved with the other fifteen or twenty per cent. of the platinum left at first, in aqua regia. Precipitating by an excess of ammonium chlorid, evaporating to dryness, and igniting, yields pure platinum. The silver may be recovered in the usual way by precipitation in

the form of a chlorid, which may be easily reduced to a metallic state by treating with a plate of zinc in acidulated water.

It is a somewhat common belief that the putting together of silver and platinum in the formation of an alloy of this kind, owing to the infusibility of platinum and the wide difference in the fusing-points of the two, is a matter of great difficulty. It should be borne in mind, however, that between the metals more or less affinity exists, especially at high temperatures; hence it is only necessary to introduce the platinum, rolled into thin ribbons, into the crucible containing the silver in a state of complete fusion, and the platinum will be observed to quickly fuse and mix with the other metal. It is sometimes thought advisable to add larger proportions of platinum than the quantity here given. This may be done by adding the platinum until the alloy becomes infusible, and this result will be attained as soon as sufficient platinum is added to raise the fusing-point of the alloy above the capacity of the ordinary melting apparatus.

Von Eckart's alloy, employed to some extent in France as a base for artificial dentures, is composed of the following proportions: silver, 3.53; platinum, 2.40; and copper, 11.71. It is very elastic (which property it does not lose by annealing), and can be highly polished.

*Silver Solders.*—When the plate to be united consists of pure silver alloyed with platinum, the solder may be formed of the standard metal (coin), with the addition of from one-tenth to one-sixth its weight of zinc, according to the proportion of platinum contained in the alloy. Silver solders are, however, generally

composed of silver, copper, and zinc, or silver and brass, in variable proportions, of which the following are examples :

	No. 1.*	
Silver		66 parts.
Copper		30 “
Zinc		10 “
	No. 2.†	
Silver		6 dwts.
Copper		2 “
Brass		1 dwt.
	No. 3.	
Silver		5½ dwts.
Brass wire		40 grs.

In putting together the constituents of silver solders, the affinity for oxygen manifested by zinc, brass, and copper, when exposed to high temperatures, should be remembered, and in order to guard against loss the mode of procedure should be as follows : The silver, placed in a clean crucible, with a sufficient quantity of borax to cover it, should be thoroughly fused, and, without permitting it to cool in the least, the zinc, brass, or copper, as the case may be, should be quickly added. Before pouring, it should be shaken or agitated to insure admixture. When cool, it may be removed from the ingot-mold and rolled into plate of, say No. 27 of the standard gauge.

The surface of standard silver may be whitened by being heated and immersed in dilute sulfuric acid. It is in this way that frosted silver is produced. The acid, dissolving the oxid of silver from the surface, leaves a quite pure superficial film.

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\* Richardson's Treatise on Mechanical Dentistry.

† *ibid.*

Silver may be deposited upon the surface of another metal by connecting the article to be silvered with the negative (zinc) pole of the galvanic battery, and then immersing it in a solution made by dissolving cyanid of silver in a solution of cyanid of potassium. The current decomposes the argentic cyanid, and the metal is deposited upon the object connected with the negative pole. During this decomposition the cyanogen liberated at the positive (copper or platinum) pole acts upon a silver plate with which this pole is connected, the quantity of silver dissolved at this pole being precisely equal to that deposited at the opposite pole ; the silvering solution is always maintained at the same strength.

## CHAPTER X.

### PLATINUM.

ATOMIC WEIGHT, 197.6. SYMBOL, PT.

PLATINUM is found in nature in flattened grains of varying sizes, more or less alloyed with palladium, rhodium, ruthenium, davyum, and iridium.\* It occurs in Brazil, Peru, Australia, and California. Russia, however, furnishes the largest supply of platinum, from the Ural Mountains. It was discovered in 1736 by Anton Ulloa, at Choco, in South America ; but, in consequence of its infusibility and unworkable nature, no use was made of it, and its presence in mining products was considered a hindrance. Dr. Wollaston devised the first practical process of working it, and in 1859 Deville and Debray published improved methods of fusing large quantities of platinum.

Wollaston's method, which consists of a series of chemical and mechanical processes of a rather complicated nature, may be thus described : The ore is first heated with nitric acid to dissolve any copper, lead, iron, or silver. It is then washed and heated with hydrochloric acid to remove any magnetic iron ore that may be present ; after which the ore is to be treated with nitro-hydrochloric acid diluted with an equal bulk of water to prevent the iridium, which is gen-

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\* A group of rare metals only found in platinum ores, and known as the "platinum metals."

erally present, from being dissolved. The proportions of acids are one hundred and fifty parts of hydrochloric to forty parts of nitric. Three or four days' digestion, aided by gentle heat, is necessary to complete solution. The suspended matter, generally consisting of iridium, is allowed to subside, when the solution may be syphoned off.

Ammonic chlorid\* is next added as a precipitant, and throws down the yellow crystalline ammonio-platinic chlorid, which is readily decomposable by heat, yielding platinum in a finely-divided state.

The liquid from which the precipitate is obtained will still be found to contain about eleven parts of platinum, together with all the associated metals. These are all thrown down by means of a plate of zinc, and washed carefully and again dissolved in nitro-hydrochloric acid. A small quantity of strong hydrochloric acid is added to avoid precipitation of lead or palladium, when precipitation of the remaining platinum may be again effected by ammonic chlorid. This precipitate will require careful washing in cold water to remove iridium, which during the process forms a double salt with the ammonic chlorid.

The next stage in the operation consists in separating the metal from the ammonia salt by ignition, and, as it is important to the success of the subsequent working that the precipitate shall remain in a finely-divided state, too high a degree of heat must be avoided, as otherwise cohesion of the particles will take place. Ignition is generally accomplished by the following means : The precipitate is heated in a graphite crucible until nothing remains but the finely-divided

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\* About forty parts.



platinum. This is powdered, should it be found somewhat lumpy, in a wooden mortar with a wooden pestle, sifted through a fine lawn sieve, and mixed with water to the consistence of a stiff paste. This is placed in a brass mold with a slightly tapering cylindrical cavity about seven inches in length, provided with a loosely-fitting steel stopper, which enters to the depth of a quarter of an inch. The mold is first oiled and set up in a vessel of water. The platinum mud is then introduced, and as it settles into the water air is displaced, and the platinum is thus made to fill every part of the mold. The water is allowed to drain, and its removal may be aided by pressure. Ultimately, however, the mold is placed in a press worked by a powerful lever, by which the mass sustains an enormous pressure, after which the plug and the column of platinum are removed by gently tapping the mold. It is then heated in a charcoal fire, in order to thoroughly dry it and to burn off any adherent oil.

The next step, which depends upon the quality of welding possessed by platinum, consists in heating the porous cylinder in a blast-furnace to white heat, when it is removed, set upright on an anvil, and hammered on the ends in order to weld the particles ; after which it is coated with a mixture of borax and carbonate of potash, and again heated for the purpose of removing traces of iron, which is dissolved by the mixture, the latter being removed by immersion in dilute sulfuric acid. The bar of platinum is now ready for use, and may be rolled or hammered.

It may readily be surmised that so imperfect a means of obtaining a solid bar of metal as the latter part of the operation just described cannot always be relied

upon for the production of a uniform and solid specimen; and, indeed, platinum prepared in this way, though of great purity, is liable to blister upon its surface, this being probably due to minute globules of air incased in the body of the ingot during the forging, which, during the conversion of the ingot into plate by means of rollers, are elongated and spread out in the form of blisters.

The dry metallurgic operations of Deville and Debray consist in heating in a reverberatory furnace about two-hundred-weight of platinum ore with an equal weight of galena (sulfid of lead). When the ore is sufficiently heated (to bright redness), portions of the galena are added and mixed with the ore by constant stirring. An equal quantity of litharge is next added, in order to supply oxygen to the sulfur of the lead ore, which passes off as sulfurous anhydrid, reducing all of the lead which combines with the platinum. After remaining in a state of fusion for a short time the upper portion is ladled off, and will be found to consist of an alloy of lead, platinum, and smaller portions of palladium and silver, the latter being introduced from the galena, which always contains more or less silver. The heavier metals of the platinum group, by their greater density, subside to the bottom.

Cupellation is now resorted to in order to separate the platinum from the lead. This consists of two distinct operations. The first is performed at the ordinary furnace-temperature, and is continued until by loss of lead the fusing-point of the remaining alloy rises to such an extent that a state of fusion can no longer be maintained. The second and final operation is performed in an apparatus which serves the

purpose of both furnace and cupel. It is formed of blocks of thoroughly burned lime. In form it may be described as a sort of basin or concavity with a similar piece for a cover. The lower part is intended for the reception of the metal ; through the center of the upper portion or cover pass the tubes for the oxyhydrogen jet, while the lower portion is provided with a lip or spout for pouring the melted metal. The tubes which pass through the top for the transmission of the two gases are generally formed of copper, with platinum tips. The outer and lower tube carries hydrogen, while the inner and upper one carries a jet of oxygen, into the middle of the flame. The tubes are furnished with stop-cocks, so that the supply may be regulated. When the object is merely to fuse some scraps of platinum, the lime-furnace is first put together, the hydrogen jet is lighted, oxygen is then turned on, and the interior of the apparatus soon becomes heated. The platinum is then introduced in pieces through a small hole at the side, and quickly fuses after entering the furnace.

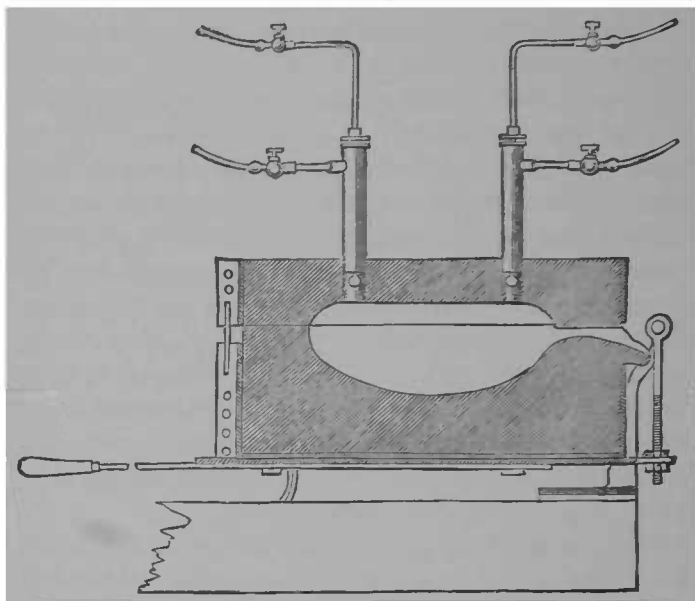
When used as a cupel the lime absorbs the impurities, and the platinum is kept in a state of fusion until all the lead is oxidized, when the metal may be poured from the lime-cupel into an ingot-mold formed of coke or plates of lime. Some difficulty may be experienced at the moment of pouring, in consequence of the dazzling white surface of the molten metal. From seven to eight pounds may be melted in this way in from forty to sixty minutes.

Although such metals as palladium, osmium, gold, silver, and lead are volatilized at the intense heat used, it has been found that platinum obtained by the Deville-

Debray method is not as pure as that obtained by Wollaston's plan.

*Properties.*—Platinum is somewhat whiter than iron. It is exceedingly infusible, requiring the flame of the

FIG. 19.



compound blow-pipe (oxyhydrogen) to render it fluid. In both the hot and cold states it is exceedingly malleable and ductile.\* It is the heaviest substance in nature, its specific gravity being 21.5, and it is ex-

\* Wollaston, in endeavoring to substitute platinum for the spider's web usually employed in micrometers, made platinum wire finer than had hitherto been obtained. This was accomplished by forming a coating of silver upon a platinum wire, and then passing it through the draw-plate, after which he dissolved the silver, leaving the platinum the  $\frac{1}{30000}$  of an inch in diameter, a mile of which, notwithstanding the high specific gravity of the metal, would only weigh a single grain.

ceeded in tenacity only by iron and copper. No single acid attacks it, and it is unaffected by air or moisture at any temperature. It is therefore of great value in the construction of chemical vessels.

At bright-red heat platinum welds quite readily, and injured vessels may be repaired in this way. In the finely-divided state, as obtained by Wollaston's process, it may be made into small vessels by pressing the pulverulent metal into suitable molds, heating and hammering to complete the welding of the particles.

Platinum possesses the remarkable property of inducing chemical combination between oxygen and other gases. Even in the compact condition it possesses this quality, as demonstrated by the familiar experiment of suspending a coil of platinum wire in the flame of a spirit-lamp, and suddenly extinguishing the flame as soon as the metal becomes entirely heated, when, by inducing the combination of the vapor of the spirit with oxygen, the wire will continue to glow. An instantaneous light apparatus has been made in which a jet of hydrogen is thrown upon a ball of spongy platinum; the latter induces combination between the oxygen condensed between its pores and the spirit-vapor, and ignition takes place.

Platinum-black, in which the metal exists in an exceedingly fine state of division, possesses this power of promoting combination of oxygen with other gases to the highest degree. In this form it is capable of absorbing eight hundred times its volume of oxygen. No combination, however, takes place between the two, the gas being merely condensed within the pores of the metal ready for combination with other bodies; hence, if a jet of hydrogen be thrown upon a small

lump of this powder, ignition ensues. During the operation of melting, platinum absorbs oxygen and gives it off in cooling, "sputtering," as silver does under like conditions.

The proper solvent for platinum is nitro-hydrochloric acid, the chlorine evolved being the active agent. Alloyed with silver, however, platinum will be dissolved in nitric acid, and when platinum is found in gold as an alloy it may be separated by quartation with silver.

*Alloys.*—Equal weights of platinum and gold afford a malleable alloy; the brilliancy of appearance characteristic of gold is, however, much lessened by the admixture. The two metals, combined in the proportions of 1 part of platinum to 9.5 of gold, form an alloy of the same density as platinum. An excess of platinum with gold yields an alloy which is infusible at ordinary furnace-heat.

The tenacity of gold is very greatly increased by admixture of platinum, while at the same time it is rendered more elastic.

Platinum and silver may be combined in all proportions, constituting alloys of greater hardness than either of their constituents, while the color is between the color of silver and that of platinum. Hot sulfuric acid will dissolve the silver from an alloy of this kind, and when one part of platinum is alloyed with ten parts of silver both metals may be dissolved by nitric acid.

Platinum and mercury do not amalgamate readily, and combination can only be effected by rubbing finely-divided platinum, such as is reduced from the ammonio-chlorid, in a heated mortar with mercury

moistened with water acidulated with acetic acid. By this means an unctuous amalgam is obtained, which has been employed in platinizing metallic objects in a manner similar to that known as fire-gilding.

The use of platinum as a constituent in alloys for dental amalgams has been almost entirely abandoned. The author found, as the result of a large number of experiments, that it rendered the alloy very brittle ; and, while its presence seemed to retard amalgamation, it increased the capacity of the alloy for mercury (see page 54).

Iridium confers upon platinum great hardness and tenacity ; indeed, the alloy resulting from this combination is so rigid that it is with the greatest difficulty it can be swaged into plates. It is, nevertheless, an alloy of great value to the mechanical dentist, as it affords a means of obtaining greater strength in artificial dentures of the "continuous-gum" class, and it has been used in the author's laboratory since 1870 in connection with vulcanized rubber, the plate being constructed of iridio-platinum, with the teeth, single or in sections, attached by means of rubber. The swaging requires the use of the zinc counter-die, and when the ridge is very prominent it is best not to attempt to carry the plate entirely over it, rather allowing the rubber to take its place. An artificial denture constructed in this way has no superior in point of strength and durability.

Nothing but pure gold should be used as a solder in uniting two pieces of platinum or iridio-platinum. Indeed, so feeble is the union between the latter and an ordinary gold solder that two pieces united by its agency may be readily torn apart with the pliers. The

addition of iridium is also of value in the construction of platinum vessels for experimental laboratory use, as the metal is thereby rendered more resistant to high temperatures, and less susceptible to the action of chemicals.

Platinum combines with tin in all proportions, and the resulting alloy is hard, brittle, and more or less fusible. Between the platinoid metals and tin, at the moment of fusing together, phenomena very suggestive of true chemical union have been observed, and if tin and platinum foils be rolled together and heated under the blow-pipe, combination takes place explosively. It is in consequence of this affinity that two such metals, one of which is infusible at ordinary furnace-temperature, while the other is readily fusible at a low degree of heat, may, with the greatest facility, be melted together to form an alloy.\*

*Oxids.*—Platinum unites with oxygen to form two compounds,—the monoxid or platinous oxid ( $\text{PtO}$ ), and the dioxid or platonic oxid ( $\text{PtO}_2$ ). The first is obtained as a black powder by digesting the dichlorid with caustic potash. The second ( $\text{PtO}_2$ ) may be prepared by adding barium nitrate to a solution of platonic sulfate. Barium sulfate and platonic nitrate are thus formed, and from the latter caustic soda precipitates one-half of the platinum as platonic hydrate, a bulky brown powder, which, when gently heated, becomes black and anhydrous. It is also formed when platonic chlorid is boiled with an excess of caustic soda, and acetic acid added. It combines with bases and dissolves in acids. Platonic oxid with ammonia forms

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\* See chapter on "Alloys."



an explosive compound, which detonates violently at about 400° F. Both oxids of platinum are reduced to the metallic state by heating to redness.

Platinic chlorid ( $\text{PtCl}_4$ ) is the most useful salt of the metal, and is the one from which all the platinum compounds are obtained. It may be prepared by dissolving scraps of platinum in a mixture of four measures of hydrochloric acid with one of nitric acid, one hundred grains of platinum requiring the presence of two ounces of hydrochloric acid. After complete solution the liquid is evaporated at a gentle heat to a syrupy consistence, redissolved in hydrochloric acid, and again evaporated to expel excess of nitric acid. The syrup-like fluid solidifies on cooling to a red-brown mass, which is deliquescent and readily dissolves in water or alcohol.

Spongy platinum is prepared by heating the yellow crystalline precipitate obtained by the addition of ammoniac chlorid.

Platinous chlorid ( $\text{PtCl}_2$ ) may be formed by heating platinic chlorid to a point somewhat above 450° F. A very high temperature reduces it to the metallic state.

*Sulfids.*—The compounds  $\text{PtS}$  and  $\text{PtS}_2$  are produced by the action of hydrogen sulfid, or the hydrosulfid of an alkali metal, on the dichlorid and tetrachlorid of platinum respectively. They are both black, insoluble substances.

*Discrimination of Platinum Salts.*—1st. A blackish-brown precipitate, insoluble in nitric or hydrochloric acid singly, will be thrown down by the addition of hydrogen sulfid ( $\text{H}_2\text{S}$ ).

2d. Ammonia or potash throws down a yellow crystalline precipitate.

3d. A brown hydrated platinic oxid is precipitated from the salts of platinum by the addition of soda, and it should be remembered that the precipitate is soluble in an excess of the soda.

4th. A deep-brown color is imparted to solutions of platinum salts by the addition of stannous chlorid, but no precipitate is obtained.

Quantitatively, platinum may be separated from other metals with which it is likely to be associated by precipitating with ammonium chlorid. This is added to the platinum solution, followed by a little alcohol. The precipitate is collected, washed with alcohol, and dried, when it is ready for weighing. Every 100 parts will contain 44.28 of platinum.

## CHAPTER XI.

### IRIDIUM.

ATOMIC WEIGHT, 198. SYMBOL, IR.

**I**RIDIUM, named from Iris, the rainbow, because of the varied colors of its compounds, has already been mentioned as occurring in the insoluble alloy from the platinum ores, and disseminated in small, hard points throughout the substance of California gold. It is also obtained when crude platinum is dissolved in nitro-muriatic acid. A gray, scaly, metallic substance is found at the bottom of the vessel, which has entirely resisted the action of the acid. This is *osmiridium*, a native alloy of iridium and osmium. The subsequent treatment for the separation of the two metals consists in reducing them to powder, combining them with an equal weight of dry sodium chlorid, and heating to redness in a glass tube, through which moist chlorin gas is allowed to pass. The tube is connected with a receiver containing a solution of ammonia. The gas is quickly absorbed, and iridium chlorid and osmium chlorid are formed. The first remains combined with the sodium chlorid, while the osmium chlorid, being a volatile substance, passes into the receiver. The contents of the tube, consisting of iridium and sodium chlorids, when cold, are dissolved with water, and mixed with an excess of sodium carbonate and evaporated to dryness. After ignition in a crucible, boiling in water, and drying, the metal may be reduced by hydrogen (at a high temperature), and

heating successively with water and strong hydrochloric acid to free it of the alkali and iron. What remains consists of metallic iridium in a finely-divided state.

*Properties.*—Iridium is an exceedingly hard and brittle metal, nearly white in color, and fusible only by the oxyhydrogen blow-pipe, by which means it has been converted into a white mass having somewhat the appearance of polished steel. It is hard\* and brittle while cold, but it is rendered somewhat malleable at red heat. Its density is about the same as that of platinum. It has been obtained in tolerably compact masses by compressing some of the metal in a very fine state and then heating to the highest point attainable in a forge-fire. The density of a sample of iridium prepared in this way will not exceed 16.0.

When reduced by hydrogen at low temperatures it dissolves in nitro-hydrochloric acid, but is rendered insoluble in all acids by exposure to white heat. It may again be dissolved by igniting it with a mixture of the chlorid of potassium and sodium in a current of chlorine.

Mr. John Holland, of Cincinnati, devised an ingenious process for the preparation of larger pieces of iridium than are generally found in nature. Some of the ore is heated to whiteness with phosphorus in a Hessian crucible, by which means complete fusion is obtained. Phosphor-iridium, as this compound may be called, is as hard as the iridosmine from which it is

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\* Its hardness is such that the hardest file will make no impression on it. In working California gold, which often contains disseminated through it small grains of the native alloy of osmium and iridium, the file is sensibly injured by contact with it, while in coining operations much inconvenience and injury are caused by its presence.

prepared, and is used for making points for the Mackinnon stylographic pen.

*Alloys.*—Platinum containing a small quantity of iridium is rendered more rigid, and is of great value as a means of strengthening continuous-gum work, by forming the backing of it, especially in partial lower sets, where, in addition to the two pieces of pure platinum covering the gums back of the natural (front) teeth, an extra piece of platinum alloyed with iridium, No. 26, may be used. It also answers well in combination with vulcanizable rubber,\* for either entire or partial cases, and though decidedly the most refractory of the various alloys employed in the dental laboratory, it may be perfectly swaged by the use of a zinc counter-die. In the construction of partial cases it may be employed for clasps, but wherever it is necessary to unite two pieces by soldering nothing but pure gold should be employed as the solder. Ordinary gold solders do not afford a strong union.

Iridium unites with oxygen, sulfur, chlorine, and iodine, to form oxides, sulfides, chlorides, and iodides.

*Discrimination.*—With ammonium or potassium chloride, iridium solutions afford a dark reddish-brown crystalline precipitate of ammonium or chloridate, the color of which, and the fact that it is reducible to soluble chlor-iridium when treated with hydrogen sulfide, distinguishes it from the corresponding platinum precipitate.

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\* See chapter on "Platinum."

## CHAPTER XII.

### PALLADIUM.

ATOMIC WEIGHT, 106.5. SYMBOL, PD.

PALLADIUM, rhodium, iridium, ruthenium, osmium, and davyum\* constitute a group of metals which possess many properties in common. They are also closely allied by natural association.

Crude platinum is a native alloy of platinum with these metals, and is the source whence they are usually obtained.† Palladium is, however, occasionally found native, in a comparatively pure state, intermixed with platinum, from which metal it may be readily distinguished by the fibrous appearance of its grains.

It is obtained at the present time chiefly from the solution of crude platinum, after that metal has been separated by precipitation with ammoniac chlorid. The remaining liquid is neutralized by sodium carbonate, and mixed with a solution of mercuric cyanid; palladium cyanid separates as a whitish, insoluble substance, which, on being washed, dried, and heated

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\* This metal, named in honor of Sir Humphry Davy, was discovered by Kern in 1877, in platiniferous sand. It was obtained from the mother liquors after the separation of platinum, palladium, osmium, and iridium, by heating them with an excess of ammonium chlorid and nitrate. A deep-red precipitate was obtained, which after calcination at a red heat left a grayish mass resembling platinum sponge. This, when fused by the oxyhydrogen blow-pipe, furnished a silver-white metal of great hardness, though malleable at a red heat, having a density of 9.39; soluble in aqua regia, but only slightly acted upon by boiling sulfuric acid.

† Palladium was, at one time, obtained in considerable quantities from Brazilian gold, with which it was associated as an alloy, but this means of supply having failed, it has become too expensive for employment in the industrial arts.

to redness, yields metallic palladium in a spongy state, which admits of welding into a solid mass in the same manner as platinum.

In appearance palladium resembles an alloy of platinum and gold wherein the proportion of the former greatly exceeds that of the latter. It possesses the qualities of malleability and ductility, but in those properties it is probably inferior to platinum. Its density differs very much from platinum, being only 11.8. It is more oxidizable than platinum, and when heated to redness in the air, especially when in a finely-divided state, it acquires a superficial film of oxid of a bluish color, which may be again reduced at a high temperature. It does not, however, oxidize in the air unless its temperature is raised to red heat, and on account of its unalterability in the air and its bright silver-white color, which is not affected by exposure to sulfuretted hydrogen, it is used for preparing the graduated surfaces of astronomical instruments and for coating silver goods. It is the most fusible of the platinum metals, and requires about the heat needed to fuse malleable iron to reduce it to a state of fluidity, in which condition it absorbs oxygen, parting with it again in cooling in the same way that silver does. It is dissolved by nitric acid, but its best solvent is nitro-hydrochloric acid. It is attacked by iodine, and may be distinguished from platinum by heating a drop of tincture of iodine upon it, when it will show a stain, while platinum similarly treated is quite unaffected.

*Alloys.*—In a finely-divided state it unites readily with mercury, and there would appear to be some chemical affinity between the two, the union being

accompanied by evolution of heat. As the amalgam cools it sets and becomes tolerably hard, and it is stated that it expands in hardening.\*

*Palladium Precipitate.*—The form in which the metal is generally used in amalgams seems to lose its affinity for mercury after long exposure to the air, and combination can only be effected by the assistance of gentle heat. Apparatus for determining the expansion or contraction of amalgams has been employed to test the expansibility of palladium amalgams. One of these, consisting of a trough having a movable end with a screw micrometer capable of noting the most minute change, indicated in one specimen of palladium amalgam an expansion of 1 in 25† of its diameter, though the amount of solid matter in this class of amalgams is very small, as it requires three parts of mercury to one of precipitated palladium.

Mr. Coleman‡ states that palladium amalgam sets very rapidly, and when mixed in large enough quantities to fill good-sized cavities all the phenomena of true chemical affinity are observed. He also gives the following description of the manner of mixing and applying the amalgam: "About as much mercury as would fill the cavity to be treated is placed in the palm of the hand, and the palladium powder very gradually added. It requires some careful rubbing with the forefinger before the two become incorporated, when it should be divided into smallish pellets, and these rapidly carried, one after another, to the cavity, each piece

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\* Hitchcock on Dental Amalgams, page 33, Transactions of the New York Odontological Society, 1874.

† British Journal of Dental Science, Vol. 1X, Part 11, July, 1888.

‡ Manual of Dental Surgery and Pathology, page 129.



being well compressed, and rubbed into the irregularities of its walls with a burnisher or compressing instrument." Mr. Coleman further states that this is probably the most durable of all the amalgams, but the most difficult to manipulate. Its surface changes to a black color, but, as a rule, it does not stain the structure of the tooth.

Palladium has been used as a constituent in dental alloys (amalgams), and when added to a gold, silver, and tin alloy it probably has about the same effect as does platinum. It has been observed, however, that dental alloys in which it is a constituent blacken to a greater extent than when it is omitted. Mr. Fletcher,\* after a series of experiments, finally abandoned its use in dental amalgams.

Silver and palladium unite in all proportions, forming alloys which retain an exceedingly brilliant surface.

Gold and palladium, in equal proportions, form a hard, gray alloy. Indeed, all the alloys formed of these two metals are exceedingly hard.

Palladium and platinum form a hard alloy, which fuses below the melting-point of palladium.

Palladium combines with antimony, bismuth, zinc, tin, iron, and lead, forming brittle alloys. With nickel it forms malleable alloys which are susceptible of high polish.

It is quite probable that palladium, either alone or alloyed with other metals, might be advantageously employed in prosthetic dentistry, but its high price practically excludes it from the dentist's laboratory.

Palladium enters into combination with chlorine

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\* See chapter on "Amalgams."

(PdCl<sub>2</sub>), oxygen (PdO and PdO<sub>2</sub>), and sulfur (PdS). When heated to redness in a stream of hydrogen gas, it possesses the remarkable power of absorbing about 643 times its volume of the gas, whereby its specific gravity is reduced to 11.06. The absorption of the gas is attended with evolution of heat, and this fact, together with the supposed constancy of composition of the hydrogenized palladium, led Graham to suppose that the product was a definite chemical compound, to which he assigned the formula PdH<sub>2</sub>. Troost and Hautefeuille, however, found the correct composition to be Pd<sub>2</sub>H.\*

*Discrimination.*—Mercuric cyanid is the chief test for palladium.† It precipitates a yellowish-white cyanid, soluble in hydrochloric acid, which is easily reduced by heat to metallic palladium, when it is ready for weighing.

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\* Watt's Dictionary of Chemistry.

† There are other reagents employed in the discrimination of palladium, —sulfuretted hydrogen, potash, ammonia and its carbonates, ferrous sulfate, and stannous chlorid. Mercuric cyanid, however, is the one generally employed in the quantitative estimation of palladium.

## CHAPTER XIII.

### IRON.

ATOMIC WEIGHT, 56. SYMBOL, FE (FERRUM).

IRON is present in nearly all forms of rock, clay, sand, and earth. It is the most widely diffused of the natural coloring ingredients, and its presence may be readily distinguished by the color which it imparts. It is found in varying proportions in plants and the bodies of animals, the blood of the latter containing about 0.5 per cent. of iron associated with its coloring-matter.

Iron seems to have been known very early in the world's history, and at a remote period instruments of agriculture and war were manufactured of it.\* Its chief ores are oxids, carbonate, and sulfids. Metallic iron† is met with in nature in the meteorites or metallic masses of unknown origin which occasionally fall to the earth.‡ The carbonates and oxids are the ores from which iron is chiefly obtained. Their reduction—the oxids especially—is exceedingly simple, and consists in merely heating them in contact with carbonaceous compounds, by which means the metal is liberated.

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\* Archæologists distinguish a Bronze Age in prehistoric times intermediate between those of Stone and Iron.

† Metallic iron, though of exceedingly rare occurrence, has been found at Canaan, in Connecticut, forming a vein about two inches thick, in mica slate.

‡ Isolated masses of soft iron, sometimes of large dimensions, have been found upon the surface of the earth in South America; they are supposed to have had a similar origin.

*Properties.*—Pure iron is white in color, extremely soft and tough, and has a specific gravity of 7.8. Iron may be regarded as possessing a greater number of valuable qualities than any other metal; hence it occupies the highest place in the useful arts. Although possessing nearly twice as much strength as the strongest of the other metals, it is yet one of the lightest, and is therefore peculiarly fitted for use in the construction of bridges, ships, etc. It is rendered so ductile by heating that it may be rolled into very thin sheets or drawn into the finest wire; and yet at ordinary temperatures it is the least yielding of the metals in common use, and may always be relied upon to afford a rigid support. An iron wire one-tenth of an inch in diameter is capable of sustaining seven hundred and five pounds. It is very difficult of fusion, and before becoming liquid passes through a soft or pasty condition. Pieces of iron pressed or hammered while in this state cohere or weld together.

The fusing-point of iron has been estimated at  $2900^{\circ}$  F. It is soluble in nitric, dilute sulfuric, and hydrochloric acids, but is not much affected by strong sulfuric. Chlorin, iodine, and bromine attack it readily. Under certain circumstances it is not acted upon by strong nitric acid. If a piece of platinum wire be kept in contact with it, it will remain in this acid for many weeks without being acted upon. Its crystalline form is supposed to be a cube. When rolled into bars or drawn into wire it possesses a fibrous texture, upon the perfection of which much of its strength and value depend. It is the most tenacious of all the metals. At red heat iron decomposes water evolving hydrogen, and is changed into the black oxide. It is a

strongly magnetic metal, but loses this quality when heated to redness.

Iron does not oxidize in dry air at ordinary temperatures, and it may be immersed in water from which the air has been carefully excluded without change. Contact with a more electro-positive metal will also prevent oxidation. Thus, fine steel instruments are sometimes packed for exportation by wrapping in thin sheet zinc. For a description of the compounds of iron and the reagents employed in its discrimination, the student is referred to Fownes's "Elementary Chemistry."

The value of iron does not depend alone upon its physical properties, for it enters into a large number of compounds which are of great use in the arts, and its chemical relation to carbon is such that the addition of a small quantity of that element converts it into steel, harder and more elastic than iron, while a larger quantity of carbon produces cast iron, which is so fusible that many useful articles may be made of it by casting.

*Steel.*—Herodotus states that among the most precious gifts presented by the Indian monarch Porus to Alexander the Great was a pound of steel, the value of which at that time has been estimated at about two hundred dollars. At a later period the manufacture of steel in its application to warlike instruments was carried to a great state of perfection in India and in the south of Europe.

Steel differs from iron in possessing the property of becoming very hard and brittle, if, when heated to bright redness, it is suddenly cooled by being plunged into water. Steel is simply iron chemically combined

with the precise amount of carbon which will produce the condition referred to, together with additional toughness. It does not, however, become decidedly steel-like until the carbon amounts to 0.3 per cent. The hardest steel contains about 1.2 per cent. of carbon, and when that proportion is exceeded it begins to assume the properties of cast iron.

There are several processes by which steel may be produced. Bars of iron imbedded in charcoal powder in a suitable crucible or chest made of some substance capable of resisting the fire are, after several hours' exposure to heat, converted into steel, the iron taking up the requisite amount of carbon. The product of this operation is called blistered steel, and is far from uniform, either in composition or texture, as portions of the bars thus produced will be found to contain more carbon than others, and the interior to be more or less porous. For the purpose of improving its quality the bars are cut into short lengths, made up into bundles, heated to the welding-point, and placed under a powerful tilt-hammer, which consolidates each bundle into one mass. This is called shear steel.

Fusing and casting steel is another process for the treatment of the blistered form, by which is produced the best and most homogeneous variety. It consists in fusing about thirty pounds of broken fragments of blistered steel in a plumbago crucible, the surface being protected from oxidation by glass melted upon it. When perfectly fluid the steel is cast into ingots, and when it is desirable to form a very large ingot, several crucibles are simultaneously emptied into the same mold. Cast steel is superior in density and hardness to shear steel, and is the form best adapted

to the manufacture of fine cutting-instruments. It is, however, somewhat brittle at red heat, and much care and skill are required in forging it. The addition to it while fused of one part of a mixture of charcoal and oxid of manganese affords a fine-grained steel, which may be cast into a bar of wrought iron in the ingot-mold, in order that the tenacity of the iron may be an offset to the brittleness of the steel when forged together, while it affords an economical compound in the manufacture of cutting-implements, the iron forming the back and the steel the edge of the instrument.

Bessemer\* steel is produced by forcing atmospheric air into melted cast iron. The carbon, which is oxidized more readily than the iron, escapes in the form of carbon monoxid, combustion of which takes place on coming in contact with atmospheric air, and sufficient heat is thus generated to keep the temperature above the melting-point of steel during the operation. The current of air is stopped as soon as the decarburation has progressed far enough, when a quantity of white pig-iron containing manganese is added to the fluid metal for the purpose of assisting the separation of gas from the melted metal. It is then ready for casting.

*Some New Iron Alloys.*—The combinations of iron with aluminum, chromium, copper, manganese, nickel, silicon, and tungsten constitute a class of alloys which are essentially new and are termed steels, and are usually designated with a prefix of the name of the particular element present, as nickel steel, chrome steel, etc.

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\* For other methods of producing steel, see Percey's, Phillips's, or Makins's works on Metallurgy.

*Aluminum Steel.*—The addition of aluminum slightly increases the tensile strength, and proportionately the elastic limit, in rolled and cast steel when the amount added is not greater than one per cent.

*Chrome Steel.*—Chromium increases the hardness, tensile strength, and elastic limit of iron, but lessens its weldability. Ferro-chrome is made by heating the mixed oxids of iron and chromium in brasqued crucibles, adding powdered charcoal and fluxes. Chrome steel is then produced from ferro-chrome by melting it with wrought iron or steel in graphite crucibles. It has been stated that the presence of chromium in steel renders it more susceptible to oxidation by exposure to air and moisture than ordinary steel. It was thought that chrome steel would admirably fill certain special requirements where great hardness and toughness is needed, as the manufacture of dental instruments, projectiles, cuirasses, etc., but there are other steel alloys coming into use which are so much better that it is probably only a question of time when it will be superseded.

*Copper Steel.*—M. Henry Schneider, of Creusot, France, obtained patents for the manufacture of alloys of iron and copper and steel and copper. This alloy can be made in crucible, cupola, or open-hearth furnace. The furnace is charged with copper scraps and cast iron mixed between layers of coke, or if a cupreous coke be employed then the cast iron is laid in alternate layers with it, and a layer of anthracite is laid over the whole. The alloy thus formed contains generally from five to twenty per cent. of copper, according to the purpose for which it is to be employed, and it is remarkable for its great strength, tenacity, and malle-



ability, properties which may still further be developed by chilling or tempering.

*Nickel Steel.*—United States patents 415,657 and 415,655, November 19, 1889, were granted M. Henry Schneider, of Creusot, France, for the manufacture of alloys of cast iron and nickel and steel and nickel respectively. The alloy of cast iron and nickel contains from five to thirty per cent. of nickel, and is remarkable for its great elasticity and strength, properties which admit of further development by the usual chilling or tempering.

The alloy of steel and nickel usually contains about five per cent. nickel, and is especially suitable for use in the construction of ordnance, armor-plate, gun-barrels, and projectiles. Some specimens of nickel steel recently produced by Carnegie, Phipps & Co., for the U. S. Navy Department, containing three-sixteenths per cent. nickel, showed, when tested, the following results: Elastic limit, 59,000 and 60,000 pounds per square inch; ultimate tensile strength, 100,000 and 102,000 pounds per square inch.

It is stated that the presence of manganese in nickel steel is most important, as it appears that without the aid of manganese in proper proportions the best results could not be obtained. Nickel steel is said to be less liable to corrode in salt water than ordinary steel, which, it may be proper to observe in this connection, is more readily acted upon by sea-water than are the more impure grades of iron.

The success of the nickel-steel armor-plate at the recent test by the U. S. Navy Department, in which the nickel-steel plates alone withstood the eight-inch chrome-steel projectiles without cracking, has had a

most important influence upon the manufacture of that alloy.

*Manganese Steel.* — The maximum of strength, toughness, and hardness is probably reached in this alloy, when about fifteen per cent. of manganese is added to steel. The chief obstacle to the commercial production of manganese steel is its extreme hardness. The working of some of the grades of this material by the ordinary methods is almost impossible.

Manganese steel is usually made by adding ferromanganese to molten Bessemer or open-hearth steel. The extreme point of brittleness in this alloy occurs in specimens containing from four to five per cent. of manganese. Extremes of atmosphere, heat or cold, do not appear to affect the properties of manganese steel. When a piece of it, heated sufficiently to be seen red hot in a dark room, is plunged into cold water, it becomes soft enough to be easily filed. Hardness is then restored by reheating to a bright red, and cooling in air.

*Hardening and Tempering.*—Hardening of ordinary carbon steel is effected by subjecting the object to extremes of temperature. The common practice is to first coat the surface of the metal with some carbonaceous substance, such as soap, to prevent scaling and oxidation of the surface. Ferro-cyanid of potassium has also been used for surface-hardening. This salt contains cyanogen ( $C_2N_2$ ), a gas consisting of twelve parts by weight of carbon and fourteen of nitrogen. This is decomposed at the high temperature which is employed, and supplies carbon to the surface of the metal. This salt is, however, better suited to the process known as case-hardening, while

in re-tempering dental instruments soap answers every requirement.

The metal is next heated to the point of full redness, and then suddenly plunged into cold water, oil, tallow, or mercury, or, in the case of small objects, is merely placed on a large piece of cold metal. It is thus rendered very hard, while at the same time it increases slightly in volume.

If hardened steel be heated to redness, and allowed to cool slowly, it is again converted into soft steel, but it may be proportionately reduced by heating to a temperature short of redness, the proper point of which may be ascertained by noting certain colors which appear on the ground or brightened surface of a steel instrument when held over a flame. This discoloration is due to the formation of a thin film of oxid, and as the temperature rises the film becomes thicker and darker, and the instrument softer. It is therefore necessary to plunge the instrument into a cold menstruum the instant the color indicating the desired degree of hardness is reached. The following table indicates the tempering heats of various instruments :

Temperature.	Color.	Use.
430° to 450° F.	Light yellow.	Enamel chisels.
470° F.	Medium yellow.	Excavators.
490° F.	Brown-yellow.	Pluggers.
510° F.	Brown-purple.	Saws, etc.
520° F.	Purple.	Wood-cutting tools.
530° to 570° F.	Blue.	When elasticity is desired.

In "letting down" or tempering dental instruments the flame of a spirit-lamp may be employed, the in-

strument being placed in it ; the flame should strike, however, some distance from the cutting-end, and when the proper color reaches the end it should be thrust into water. Another very convenient means of effecting the same result consists in heating an iron bar to redness at one end, and then fixing it in a vise. The object to be tempered is placed in contact with this until the desired tint appears.

Steel when fractured shows a fine silky appearance of the broken surface. Overheating, however, deprives it of carbon, when the fractured surface presents a coarse, granular condition, showing that it is unfit for use for fine cutting-instruments.

Case-hardening consists in conferring the hardness of steel upon the external surface of iron objects which are to be subjected to considerable wear, such as gun-locks, etc., and is accomplished by heating them in some substance rich in carbon (such as bone-dust, cyanid of potassium, etc.), and afterward chilling in water. The body of the piece so treated retains the toughness of iron.

Malleable iron is produced by a process the reverse of that employed in case-hardening. It consists in heating the object, usually made of cast iron (when great softness and tenacity are required), for some hours in contact with oxid of iron or manganese, by which its carbon and silicon are removed.

A steel instrument may be readily distinguished from iron by placing a drop of nitric acid upon it, a dark stain being produced upon steel by the separation of the carbon.

## CHAPTER XIV.

### MERCURY.

ATOMIC WEIGHT, 200. SYMBOL, HG (HYDRARGYRUM).

**M**ERCURY (quicksilver) has been known from a very early period. It is the only metal which is liquid at ordinary temperatures, but it becomes solid at 39° F. below zero. It is frequently found in nature in the metallic state, and it is probable that the first supplies of the metal were from this source. The ancients distinguished between such mercury and that obtained by reduction from the ores by designating the native metal as *argentum vivum* and the reduced as *hydrargyrum*,—a fact which has led some to doubt whether they were believed to be the same metal.

The sources of mercury are cinnabar, or mercuric sulfid (the ordinary ore from which the metal is obtained); horn quicksilver, or native calomel; native amalgam of silver and mercury, sometimes found trickling from crevices in the ores. It is also occasionally found in globules disseminated through the native sulfid.

*Occurrence.*—It is found in considerable quantities in Almaden in Spain, Idria in Austria, and has been found in great abundance and of remarkable purity in California and Australia. The metal is extracted from the sulfid at Idria by roasting the ore in a kiln, which is connected with an extensive series of condensing-chambers built of brick-work. The sulfur

is converted by the air in the kiln into sulfurous acid gas, while the mercury passes off in vapor, and is condensed in the chambers. The greater portion of the mercury of commerce is produced at the Austrian mine at Idria, whence it is exported in bottles of hammered iron, containing seventy-five pounds each, in a state often nearly, though never quite, pure. It is, however, frequently, when purchased in small quantities, adulterated with tin and lead. The presence of debasing metals such as these may be detected by scattering a little upon a clean glass plate, when it "tails" or leaves a track upon the glass. Lead, which is its most frequent impurity, may be removed by exposing the mercury in a thin layer (in a broad, shallow dish) to the action of nitric acid diluted with two parts of water, which should cover its surface and be allowed to remain in contact with it for several days, with occasional stirring. The lead is thus oxidized by the acid, and after digestion may be washed away.

Distillation is the means most frequently recommended for the purification of mercury, but it is now regarded as an uncertain one, since, if zinc or bismuth be present, they will be sure to distil over into the receiver with the mercury.

In distilling or redistilling mercury a strong glass retort should be used, in size corresponding with the quantity of the metal to be operated upon,\* and filled one-third with mercury, upon the surface of which is placed a layer of clean iron filings. The retort should be imbedded in a sand-bath, with the neck made to incline so as to dip below the surface of the water,

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\* For quantities exceeding two or three pounds iron retorts are employed.

with which the receiver is half filled ; and, in order to facilitate condensation of the metallic vapor, the receiver should be surrounded by cold water. Should there be a film of oxid upon the surface of the distilled mercury, a small quantity of hydrochloric acid will dissolve it, when the mercury may be washed and dried at a moderate heat. Another and better method is to substitute coarsely-powdered cinnabar for the iron filings. The sulfur liberated from the former converts foreign metals into sulfids, while the mercury present is liberated.

Probably the most certain means of obtaining mercury free from admixture of other metals is to operate upon one of the salts of mercury ; as, for instance, the red oxid, the bichlorid (corrosive sublimate), or pure vermilion. These are readily decomposed by heat, and when the red oxid is employed, simple distillation is sufficient. Should the metal after distillation show a film of oxid, the latter may be easily removed with dilute nitric acid slightly warmed. Where vermilion or the chlorid is to be reduced, the distillation will be greatly facilitated by the addition of one part of lime.

It is important that the mercury employed for dental purposes should be quite pure, and doubtful specimens may be effectually freed of the presence of the adulterating metals named by the following very simple means : A small quantity of mercurous nitrate is dissolved in water, and into this the impure mercury is placed. The salt will be decomposed, the adulterating metals oxidized, and they will be replaced by the mercury of the salt. The same result may also be attained by digesting in a solution consisting of one part of nitric acid and eight parts of water for several

hours at a temperature of  $130^{\circ}$  or  $140^{\circ}$  F. The mercury should be placed in a flask or glass dish with a broad, shallow bottom, and will require frequent shaking or stirring. The dilute acid has little or no effect upon the mercury, while it readily dissolves and combines with the impurities.

Another very simple means, said to have been devised by Dr. Priestley, has frequently been employed in purifying mercury. It consists in placing the metal with some fine-ground loaf-sugar in a bottle, which, after being securely corked, is vigorously shaken for a short time; it is then opened and air blown in by means of a bellows; again stopped and shaken as before, and, after repeating this treatment three or four times, the mercury is filtered through a cone made of smooth paper, with a fine pin-hole at its apex. The sugar, to which the oxids of foreign metals adhere, remains behind.

The method of filtering mercury through chamois-leather is to most dentists a familiar means of excluding a superabundance of mercury from amalgams, but is not to be relied on as a means of affording pure mercury.

*Properties.*—As before stated, mercury is fluid above a temperature of  $-39^{\circ}$  F. Below that point, however, it solidifies, and may be hammered or welded like other metals. During solidification it contracts and exhibits octahedral crystals. When pure, the fluid metal is exceedingly lustrous. It boils at about  $660^{\circ}$  F. It is volatile even at the ordinary temperatures, and this property is greatly increased by heat. There have been curious illustrations of the disposition to assume a state of vapor which this



metal evinces.\* It is readily soluble in strong nitric acid, but is dissolved in sulfuric acid only by the assistance of heat. Hydrochloric acid has no effect upon it

When shaken in air, or rubbed with grease, turpentine, or other substances, such as sugar, chalk, etc., mercury loses its metallic appearance, and is converted into a gray mass, as in mercurial ointment, etc. This was formerly regarded as an oxidation of the metal, and the belief was probably favored by the fact that mercury, in a state of fine division, becomes active for therapeutic purposes. The microscope, however, has revealed that such preparations are composed of metallic globules of about  $\frac{1}{750}$  of a line in diameter.

Mercury amalgamates more or less readily with gold, silver, tin, zinc, lead, bismuth, cadmium, potassium, etc., and with a greater degree of difficulty with platinum, palladium, and copper. In some instances combination between mercury and other metals takes place with considerable violence, as in the case of potassium, in which light and heat are developed. Many of the amalgams become solid and crystalline, as illustrated in dental amalgams, and for the most part they may be looked upon as definite compounds. Indeed, a native compound of mercury and silver has been found crystallized in octahedra and other forms of the regular system. The liquid amalgams are probably in many instances solutions of definite compounds in an excess of mercury; if these are pressed through chamois-leather the mercury is excluded,

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\* Burnet relates an instance in which some mercury in leather bags, forming part of the cargo of a ship, escaped into the bilge of the vessel. An elastic fluid was soon evolved, which covered every metallic article on board, while the crew, to a man, were salivated.

carrying with it but a small portion of the other metals, while a solid amalgam, frequently of definite atomic constitution, remains behind.

*Compounds.*—Mercury unites with oxygen to form mercuric and mercurous oxids, both of which are highly poisonous. With chlorin it forms two compounds, mercuric chlorid ( $\text{HgCl}_2$ ) commonly called corrosive sublimate, and mercurous chlorid ( $\text{Hg}_2\text{Cl}_2$ ), familiarly known as calomel. Mercuric chlorid is a valuable germicide, and as such is extensively used by dentists in the treatment of devitalized teeth. With iodin, mercury forms two compounds, mercuric iodid ( $\text{HgI}_2$ ), and mercurous iodid ( $\text{Hg}_2\text{I}_2$ ). The former is also regarded as a valuable antiseptic agent. With sulfur, however, mercury combines to form sulfates and sulfids. Of the latter we have mercuric sulfid ( $\text{HgS}$ ), a compound of great interest to dentists in consequence of its extensive use as a coloring pigment in vulcanizable rubbers and celluloid. It is the most common ore of mercury, and, as such, is termed cinnabar; when produced artificially it is known as vermilion. The best quality of the latter is made by the Chinese. Their process of manufacturing, for a long time a secret, consists in stirring a mixture of one part of sulfur and seven parts of mercury in an iron pot; chemical union takes place, the result of the combination being a black powder. This is divided into small lots, which are emptied separately into suitable subliming pots, heated to redness. When a sufficient quantity has been placed in the pots they are covered up, and the heat is continued for thirty-six hours, with occasional stirring by means of an iron rod passed through the lid. Lastly, the pots are broken,

and the vermilion adhering to the upper portions levigated and dried. It may also be formed by rubbing three hundred parts of mercury with one hundred and fourteen parts of flowers of sulfur, moistened with a solution of caustic potash. The resulting product, which is black, is then digested at about 120° F. with seventy-five parts of hydrate of potash and four hundred of water, until it acquires a fine red color.

Vermilion may be adulterated with red lead, disulfid of arsenic ( $As_2S_2$ ), ferric oxid, brick-dust, or any cheaper substance of a similar color ; and the discomfort sometimes caused by wearing vulcanized rubber artificial dentures may be in part due to the presence of such deleterious substances as the arsenic and lead salts referred to.

Vermilion is an inert mercurial compound,\* and is quite insoluble in either nitric, sulfuric, or hydrochloric acid. It is unaffected by water, alcohol, or the alkalies. Nitro-hydrochloric acid (aqua regia), however, dissolves and converts it into corrosive sublimate ( $HgCl_2$ ), and by exposure to a temperature of 600° F. vermilion is decomposed, and the reduced metal may be collected in globules by condensing the vapor.

Pure vermilion, in combination with rubber, is not likely to produce deleterious effects when worn in the mouth, nor is it probable that this compound can be decomposed chemically and converted into a poisonous salt of mercury by mere contact with the saliva. The mechanical dentist will, however, do well to avoid the use of nitro-hydrochloric acid in removing tin foil from the surface.

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\* In the less civilized countries the ancients used cinnabar to paint their bodies, without any bad effects. Makins, p. 128.

Regarding the presence of free mercury in rubbers before or after vulcanizing, Prof. Austen stated that the researches of Prof. Johnston with the microscope, and of Prof. Mayr by chemical analysis, failed to discover the slightest trace in samples of that which had been used by him for several years. Prof. Wildman observed that sulfur sublimed during vulcanization, but did not find the smallest trace of free mercury.\* Prof. Austen failed by mechanical force to press out any metallic globules, and during his entire experience with indurated rubber as a base for artificial dentures never, even with the microscope, detected the slightest particle of metallic mercury upon the surface of any finished piece.

If it is true, as some assert, that free mercury has occasionally been observed in rubber, then its presence must have been due to the use of an imperfect quality of vermilion; but that the latter, when pure, is ever reduced during the process of vulcanizing, or by wearing in the mouth, is not at all probable.

The modified condition of that portion of the surface of the mouth in contact with the rubber plate, often accompanied by a sensation of heat, has been attributed to an electrical action, due to the fact that rubber, "like sealing-wax, is a powerful negative electric."†

The real solution of the question, however, will probably be found in the following conditions: 1st. The non-conducting quality of the substance. 2d. The rough condition of the surface, due to carelessness or want of skill in construction. 3d. Want of

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\* Harris's Principles and Practice of Dentistry, p. 682.

† *Ibid.*, p. 681.

care on the part of the wearer, in not frequently cleaning the piece of portions of food and the secretions of the mouth, which are likely to undergo chemical change by long confinement in contact with the tissues, and thus become irritants.

The author has frequently noticed this inflamed condition where the denture was of gold or silver, but always in cases where the plate was seldom removed or cleansed. It is true, however, that the trouble referred to is more common in rubber or celluloid work ; but in both of these there are more conditions favoring such a result than are found in a metallic denture. The facts that the symptoms are not constant, and that by far the greater number of mouths in which rubber or celluloid is worn are not in the least affected by it, would seem to confirm this view.

*Discrimination.*—The presence of the soluble salts of mercury may be detected by Reinsch's test,\* which consists in placing a clean strip of copper in the solution ; metallic mercury will be immediately deposited upon it, giving it a silvery-white appearance. The strip of copper is then heated in a glass tube, by which the mercury is sublimed, and may be detected in the form of minute globules adhering to the sides of the tube after condensing.

Insoluble compounds of mercury may be detected by placing a small portion in a glass tube and covering with a layer of dry sodium carbonate, and then heating. If mercury be present, it will separate and condense in globules in the cool parts of the tube. This test is based on the fact that all mercurial compounds are decomposable by a temperature of ignition.

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\* See works on chemistry.

Mercury is also precipitated from its soluble combinations by a solution of stannous chlorid used in excess.

Hydrogen sulfid and ammonium sulfid produce in solutions, both of mercuric and mercurous salts, black precipitates insoluble in ammonium sulfid. The quantity of the reagent should be sufficient to produce complete decomposition; otherwise, a white precipitate will be formed, consisting of mercuric sulfid, with the original salt. An excess of hydrogen sulfid, however, instantly turns the precipitate black. This reaction is regarded as characteristic of mercuric salts.

Caustic potassa or soda, when added to solutions of mercuric salts, produces a yellow precipitate.

Ammonia or ammonium carbonate produces a white precipitate insoluble in excess.

Potassium or sodium carbonate causes a red-brown precipitate.

Potassium iodid throws down a bright scarlet precipitate, soluble in excess either of the mercuric salt or of the alkaline iodid.

## CHAPTER XV.

### COPPER.

ATOMIC WEIGHT, 63.4. SYMBOL, CU (CUPRUM).

COPPER is a metal with which mankind has been acquainted from the most remote periods, and probably the first metallic compound employed was copper alloyed with tin (bronze), of which many relics in the form of arms, ornaments, and domestic implements, evidently belonging to an early period in prehistoric times, are still to be found.\* It is probable, however, that the production of the pure metal is an operation of a more recent date.

Copper ores are found in many parts of America and Europe. In some parts of the United States the native metal is found in immense masses many hundred pounds in weight, sometimes slightly intermixed with silver. Nothing is certainly known of the origin of these, but they are supposed to have been formed from the cupric sulfid, which, by exposure to air and moisture, was converted into sulfate, and then, by electro-chemical agency, reduced to the metallic state.

There are several ores which yield copper. The one most commonly employed, however, is copper pyrites, a combination of sulfid of copper and iron. The blue and green carbonates, known respectively as azurite and malachite, are beautiful minerals, extensively used in Russia and Bohemia in the manufacture

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\*The epoch marked by the use of bronze is known in archæological chronology as the Bronze Age.

of ornamental objects. They contain upwards of fifty per cent. of copper.

The process of obtaining copper from an ore, such as copper pyrites, may be thus briefly described : The ore is heated in a reverberatory furnace for the purpose of converting the iron sulfids into oxid. The copper, which remains unaltered, is then heated with a siliceous sand, which combines with the iron oxid to form a slag, and separates from the heavier (copper) compound. By repeating this process the iron is finally got rid of, when the copper sulfid begins to decompose in the flame-furnace, parting with its sulfur and absorbing oxygen. The resulting oxid is, however, reduced by the aid of carbonaceous matter and a high degree of heat.

*Properties.*—Pure copper may be obtained by decomposing a solution of pure sulfate of copper in the galvanic current. If the negative wire be attached to a copper plate immersed in the solution, the pure metal will be deposited on it, and may be readily stripped off.

The chief value of copper in the useful arts is due to its great malleability, in which quality it is only exceeded by gold and silver. It fuses at about  $2000^{\circ}$  F It expands in solidifying, and absorbs oxygen very much in the same manner as silver does under similar conditions. In tenacity copper ranks next to iron, as a copper wire of one-tenth of an inch in diameter will support about 385 pounds. Its power of conducting electricity is nearly equal to that of silver, while in the transmission of heat it is surpassed only by silver and gold. It is readily soluble in nitric acid, but in sulfuric acid only with the assistance of heat.



Hydrochloric acid attacks it slowly, and in vacuo is inactive. The specific gravity of copper is 8.93. For the compounds of copper with the non-metallic elements the student is directed to Fownes's, Bloxam's, and other works on chemistry.

*Amalgams.*—Copper does not readily unite with mercury without the assistance of heat. There is, however, an amalgam of pure copper and mercury extensively used in Europe under the name of Sullivan's amalgam. Its preparation is as follows: Pure copper in a finely-divided state is obtained by boiling a concentrated solution of cupric sulfate with distilled zinc until the blue color of the salt disappears, when the zinc should be removed. The copper, which will be found in a pulverulent mass at the bottom of the vessel, should be washed with dilute sulfuric acid, subsequently in hot distilled water, and dried. It is then moistened with a solution of nitrate of mercury, by which means the copper becomes completely coated with mercury. The mercury is then added to it to the extent of twice the weight of copper (3 of copper to 6 of mercury). It is then rolled into small, lozenge-shaped pieces, which become quite hard, and are supplied to the profession in bottles containing an ounce or more. This amalgam possesses the property of softening with heat and again hardening, and when employed as a filling-material one of the lozenge-shaped pieces is placed in a small iron spoon made and sold for the purpose, and heated over the flame of a spirit-lamp until small globules of mercury are driven to the surface, when it is placed in a small glass or porcelain mortar and rubbed into a smooth paste. Some recommend washing with a weak solution of

sulfuric acid, or soap and water, and lastly with clean water alone, to remove the last traces of either acid or soap, and finally squeezing through chamois-leather to exclude surplus of mercury, when it is ready to be introduced into the cavity. It requires several hours to harden. Mr. Fletcher says of this amalgam that "it is an absolutely permanent filling, as the copper salts permeate and perfectly preserve the tooth." It is said to be quite insoluble in the mouth. It, however, becomes intensely black, and imparts a most objectionable stain to the teeth.

According to Watt's "Chemical Dictionary," the specific gravity of pure copper amalgams is the same after hardening as before, "hence the presence of copper in amalgam alloys lessens their contractibility."

It is said\* that the tendency of copper amalgam to discolor may be lessened by careful attention to its preparation. The older way of preparing it was by precipitating copper from a solution of cupric sulfate, with mercury at the bottom of the vessel that contained it, by stirring the fluid with a bar of zinc; but a better way, and one now employed, is to substitute a clean iron bar for the zinc, and leave it from twelve to twenty-four hours in a jar containing the solution. The iron bar becomes covered with a dull red flocculent precipitate of copper. When a sufficient quantity of the precipitate is formed it is collected into another jar, and well washed with a stream of cold water until it becomes quite clean. It is then ground in a mortar until it begins to amalgamate, the amalgamation being hastened by hot water slightly acidulated with sulfuric acid, which will also remove traces of iron. It should

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\* Mr. E. P. Collett, *British Journal of Dental Science*, April 15, 1890.

next be washed in liquor ammonia to neutralize traces of acid, and must then be thoroughly triturated in a mortar until thorough amalgamation has been effected. The amalgam should be rolled into small pellets, and allowed to set for twenty-four hours before using.

The expectations of valuable therapeutic qualities in copper amalgams have not been realized. Drs. C. D. Cook and W. St. G. Elliott, of London, found by experiment that copper amalgams shrunk more than simple alloys of tin and silver, and the opinion seems to be gaining ground among those who have recently somewhat eagerly adopted it as a filling-material, that it is a very uncertain agent, and that "whatever antiseptic influence it has, it does not prevent decay from beginning and progressing directly in contact with it."\*

*Alloys.*—Copper unites readily with all other metals, and many of the resulting alloys are of great value in the industrial arts,—of even more value than the pure metal. It is added to silver for the purpose of conferring sufficient hardness upon the latter to enable it, in the form of coin or plate, to withstand the attrition to which such articles are exposed. The formation of a perfectly uniform alloy of silver and copper is a process attended with some uncertainty, owing to a tendency on the part of the copper to separate and pass off toward the edges as the ingot solidifies. Thus, in silver coins one portion of the piece will frequently be found to contain more copper than another.

The decimal proportions of copper and silver in

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\*Dr. Howe, in discussions of J. Allen Osmun's paper entitled "Some Observations on the Use of Copper Amalgams," read before the New York Odontological Society, published in the International Dental Journal for July, 1892.

standard silver (coin) of several different nationalities are as follows :

Of the United States	silver 900, copper 100.
“ France	“ 900, “ 100.
“ England	“ 925, “ 75.
“ Indian rupees	“ 947, “ 53.
“ Germany—Prussian thalers	“ 811, “ 189.
“ Prussian silver groschen	“ 283, “ 717.

The properties conferred upon gold by the addition of copper are similar to those imparted to silver. These have already been alluded to on page 181. The decimal proportions in the gold coins of the United States, France, and Holland are : gold, 900 ; copper, 100 ; while English coins are composed of 916.6 of gold and 83.3 of copper. In coin-gold malleability is not greatly interfered with. Gold may, however, be rendered brittle by large proportions of copper, or when the latter is impure.

Copper and platinum form an alloy, when the proportions are equal, of nearly the same specific gravity and color as gold. Copper also unites with palladium to form a light, brassy alloy. By admixture with lead or bismuth copper is rendered quite brittle. The principal alloys in which it forms a leading ingredient are brass, bronze, and German-silver.

Aluminum bronze is formed of pure copper alloyed with from 2.5 to 10 per cent. of aluminum. It is quite malleable, and has a fine, rich, golden color. Phosphor-bronze is copper combined with from three to fifteen per cent. of tin and from one-quarter to two and a half per cent. of phosphorus. Other metals, such as silver, nickel, cobalt, antimony, and bismuth, frequently enter into the composition of bronzes.

Copper in small quantities (from 5 to 7 per cent.) is said by Mr. Fletcher to confer upon amalgams the quick-setting property obtained by the addition of platinum. It is, however, considered inferior to platinum as a constituent in dental alloys; but in the absence of platinum, amalgams are improved by the addition of a small proportion of copper.

It is stated\* that an alloy of tin 10, silver 8, gold 1, copper 1, has been extensively used (in England probably) under the names of gold amalgam and platinum amalgam.

Hydrogen sulfid ( $H_2S$ ) and ammonium sulfid, when added to a copper solution, afford a brownish-black cupric sulfid.

Caustic potash throws down a pale-blue precipitate of cupric hydrate, which changes to a blackish-brown anhydrous oxid on boiling. Ammonia also gives a blue precipitate, soluble in excess, affording a deep purplish blue solution.

Potassium ferrocyanid gives a red-brown precipitate of cupric ferrocyanid. It may also be detected in very weak solutions by placing a drop on a slip of clean platinum foil. A point of zinc is then dipped in so as to touch the foil, and instantly a spot of reduced copper appears.

A green line is imparted to the oxidizing flame of the blow-pipe when a copper salt is heated in it. It also communicates a green tint to borax when heated with it.

There are several methods which may be advantageously employed for the estimation of copper. The operations of the dentist, however, are chiefly

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\* Fletcher.

confined to the examination of amalgam alloys. The alloy should first be acted upon by nitric acid ; silver, if present, may then be recovered in the form of chlorid ; after which the copper may be precipitated from the remaining solution either as oxid, sulfid, or in the metallic state. When attempting the estimation of an alloy, a qualitative examination should first be made (page 66), and if the solution to be examined is found to contain no other metal whose oxid is thrown down by caustic potassa, an excess of that agent is to be added. In the resulting precipitate, when boiled, washed, dried, and weighed, every one hundred parts may be estimated as containing 79.85 per cent. of metallic copper.

When hydrogen sulfid or ammonium sulfid is employed as the reagent, the resulting cupric sulfid is usually oxidized by nitric acid, and again precipitated by potassa, so as to estimate as oxid.

The estimation as metallic copper is accomplished as follows : Place in the solution contained in a platinum dish a piece of zinc, adding also a little hydrochloric acid. The electrolyzing action instantly commences, and continues until the solution is colorless and the zinc completely dissolved. The finely-divided metallic copper will be found at the bottom of the vessel. This is to be well washed, dried, and weighed.

## CHAPTER XVI.

### ZINC.

ATOMIC WEIGHT, 65.2. SYMBOL, ZN.

THE ancients were undoubtedly acquainted with an ore (probably cadmia\*) which they employed with copper to form brass. Many objects of ancient manufacture, analyzed at different times, have been found to contain zinc.† The extraction of the metal itself, however, is probably a modern discovery.

Metallic zinc is never met with in nature. The principal ores are the red oxid—the sulfid of zinc (blende) and the native carbonate (calamine). The latter is the most valuable of the zinc ores, and is preferred for the extraction of the metal. It is first roasted to expel water and carbonic acid; then mixed with fragments of coke or charcoal, and distilled at a full red heat in an earthen retort. Carbon monoxid escapes, while the reduced metal volatilizes and is condensed by suitable means.

*Properties.*—Zinc is a brittle, crystalline metal, with a density varying from 6.8 to 7.2. Until about the commencement of the present century the valuable property possessed by this metal, of becoming quite malleable between 248° and 302° F., was not known; hence, prior to that discovery it was but little used in the industrial arts. Between these degrees of heat it

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\* An ore used by the ancients, containing cadmium and zinc.

† Phillips made a number of analyses of such objects, all of which showed the presence of zinc.

may be rolled or hammered without the least danger of fracture. Sheet zinc of commerce is manufactured by this means, and it retains its malleability when cold. Zinc fuses at  $773^{\circ}$  F. (below red heat). At a bright red heat it boils and volatilizes, and if heated in air combustion takes place, during which it unites with the atmospheric oxygen with brilliant incandescence. At  $410^{\circ}$  F. zinc is so brittle that it may be powdered in a mortar.

*Alloys.*—With mercury zinc forms an exceedingly brittle amalgam. The two combine in the cold state, but union is greatly facilitated by heating. Zinc is occasionally employed as a constituent in dental alloys. An amalgam has been suggested, the proportions of which are “approximately” given as, tin, 50 odd; silver, 30; gold, 5 to 7; zinc, 2 to 4; and recent experiments with it have proved so satisfactory that it has to a certain extent taken the place of platinum in dental amalgams.

Added to silver, in the proportion of 2 of zinc to 1 of silver, a nearly white, malleable alloy results.

The color of gold is heightened by the addition of zinc, while its malleability is greatly impaired. Makins states that gold rendered standard by zinc is a greenish-yellow, brittle alloy, with a specific gravity above the mean.

Combination between zinc and platinum or palladium may be effected at a comparatively low temperature, and it is accompanied by evolution of light and heat. It is stated that an alloy of 16 parts of copper, 7 of platinum, and 1 of zinc closely resembles 16-carat gold, is quite malleable, does not tarnish in air, and is capable of resisting cold nitric acid.



Zinc and lead mix with each other to a very limited extent. If equal parts of the two metals are melted together and allowed to cool, they will be found to have separated into two layers, the upper, and consequently the lighter one, zinc, retaining 1.2 per cent. of the lead, while the lower layer consists of lead alloyed with 1.6 per cent. of zinc. The necessity of carefully keeping these two metals separate in all molding operations in the dental laboratory will readily be appreciated, as a failure to observe precaution in this direction will be followed by vexatious consequences. If by accident lead becomes mixed with the zinc used for dies, the lead, by its greater specific gravity, will settle to the bottom and fill up the deeper portions of the sand matrix representing the alveolar ridge, the most prominent part of the die. This may not be discovered until an attempt to swage is made, when the die will be found to be totally unfit for the purpose. In such cases the mixed metal should be discarded and new zinc substituted.

Zinc and tin unite in all proportions without difficulty. Alloys of zinc and tin are frequently employed in casting dies for swaging plates. Richardson\* gives a formula for an alloy consisting of zinc 4 parts, tin 1 part; which, he states, fuses at a lower temperature, contracts less in cooling, and has less surface-hardness than zinc. Fletcher, however, states that all alloys of zinc and tin are superior to zinc alone for dies. The impression from the sand he believes to be much finer, and the shrinkage in cooling greatly reduced. Zinc 2, tin 1, is given as the best proportion.† Makins states

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\* Mechanical Dentistry.

† Practical Dental Metallurgy, p. 69.

that zinc and tin, when combined in equal proportions, form a white, hard alloy, not very malleable or ductile, which is capable of being worked as readily as brass.

Zinc and copper unite in various proportions to form many different grades of brass, known respectively as pinchbeck, Manheim-gold, similar, Bath-metal, Prince Rupert's metal, Muntz's sterro, Gedge's and Aich's metals. German silver and the Chinese alloys known as pacfong and tutenag are also alloys of zinc and copper, with the addition of nickel.

*Dies and Counter-Dies.*—Zinc is the metal most commonly employed in the formation of dies for swaging plates, and is superior to any of its alloys.\* Another important application of zinc is in the formation of counter-dies. The die is placed in the iron ring when a Bailey flask is employed, or invested in the molding-sand and then surrounded by a suitable iron ring in the old-fashioned way. The zinc is then heated and poured in upon the zinc die just at the moment of complete fusion. Should the metal be accidentally allowed to remain on the fire too long, and thus reach a higher temperature than is necessary, it should not be poured until it begins to solidify at the edges. The belief seems to be pretty general that melted zinc cannot be poured upon a zinc die without causing cohesion,† but if the necessary precaution regarding the proper temperature at which the metal is poured is observed, it is

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\* The author has not found the alloys of zinc and tin to be, in any respect, superior to zinc alone for dies.

† If the melted metal be poured, at a temperature of 800° F., upon a die having a temperature of 70 F., the fused zinc, by contact with the iron ring and by radiation, will lose heat enough to cause its temperature to fall far below the fusing-point, and it will probably not impart to the die more than 400° F.

impossible for union to take place, and when cool the die and counter-die will separate quite as readily as though the latter was of lead. It seems strange that this valuable expedient for the dental laboratory has not found a place in the text-books on mechanical dentistry. It frequently occurs that the zinc die and lead counter-die are totally inadequate to bring a plate (particularly if the latter is of platinum-gold or iridium-platinum) into perfect adaptation to all parts of a model, especially where the palatal arch is very deep and the rugæ are prominent.

The zinc counter-die is also of especial service in partial cases where a number of teeth remain. These are cut off from the plaster model previous to molding within one-sixteenth of an inch of the margin of the gum, so that a sufficiently distinct impress may be made in the plate to serve as a guide in filing the latter to fit around the natural teeth.

Where the swaging is likely to be attended with difficulty, at least three sets of dies and counter-dies should be made. The most imperfect of these should be furnished with a lead counter-die, and used as a preliminary die upon which to start the plate. The next in quality may be used with the zinc counter-die, and the nearest perfect of the three, with a lead counter, reserved as a finishing-die. When the plate, by means of the horn or wooden mallet and some preliminary swaging with a light hammer, has been made to assume somewhat the form of the die, and has been carefully carried past the stage when pleating or wrinkling of the plate is likely to occur, it should be trimmed to the proper dimensions, annealed, and placed between the die and zinc counter-die, and at

first gently tapped with a hammer until the die passes well into the counter-die, when one or two sharp blows with a heavy hammer, either upon the die or its counter, will carry the plate into perfect adaptation to all parts of the former. Some slight compression, however, of the prominent points of the die is likely to occur in the use of the zinc counter, so that it will be necessary to anneal and give the plate two or three sharp blows between the finishing-die and its lead counter-die; after which it will be found to perfectly fit the mouth, without any attempt to compensate for contraction of the zinc.\* It will be seen that the zinc counter-die is not intended to supersede, but is merely used as an adjunct to, the lead counter, and there is probably no better means of carrying the plate to the deep parts of the model, and of obtaining a sharp, well-defined impress of the rugæ and prominent parts of the model.

Zinc will, under favorable conditions, unite with iron, and it frequently attacks the cast-iron ladle in which it is melted, and may penetrate the side and escape into the fire. Accidents of this kind, however, may be avoided by coating the inside of the ladle with whiting.

*Compounds of Zinc.*—The oxid and the chlorid are the compounds of this metal most frequently employed by dentists. The first forms the chief ingredient in the plastic filling-materials known as oxychlorids and oxyphosphates. Zinc oxid is a white powder, the product of the combustion of the metal. It turns yellow on heating, but resumes its

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\* The subject of shrinkage of zinc when used for dies in forming metallic plates has been fully referred to on page 23.

pure white color on cooling. Chlorid of zinc, prepared by acting upon the metal with hydrochloric acid or by heating metallic zinc in chlorine, is a fusible, deliquescent substance, quite soluble in water and alcohol.

Oxychlorid of zinc, the well-known filling-material, consists of a powder and a fluid. The first is prepared by various formulæ. One in common use is as follows: Grind together in a mortar borax 2 grains, fine silex 1 grain, oxid of zinc 30 grains. When thoroughly mixed these are placed together in a small crucible and heated to bright redness. This is called the frit, and when cool requires grinding to again reduce it to a pulverulent state. It is then thoroughly mixed with three times its weight of calcined oxid of zinc. The fluid usually employed with the powder consists of chlorid of zinc diluted with water in the following proportions: Deliquesced chlorid of zinc, 1 ounce; water, 5 or 6 drams. The oxyphosphate powders are similar mixtures.\* The fluid, however, is prepared by dissolving in pure water some glacial phosphoric acid, and then evaporating until the solution attains the consistence of glycerin.

The presence of zinc in solution is distinguished by the following reactions: A white precipitate soluble in excess of the alkali is obtained by the addition of caustic potash, soda, or ammonia, and zinc is distinguished from all other metals by ammonium sulfid, which precipitates white sulfid of zinc, insoluble in caustic alkalies.

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\* Oxid of zinc, 200 parts, silex 8, borax 4, ground-glass 5, levigated under water to insure complete admixture, then dried by evaporation, calcined at a white heat, and pulverized, has been found to be equal in durability and working qualities to any of the numerous oxyphosphates now in the market.

## CHAPTER XVII.

### CADMIUM.

ATOMIC WEIGHT, 112. SYMBOL, CD.

**C**ADMIUM, a metal closely allied to zinc, was discovered by Stromeyer and Hermann in 1817. It does not occur in the metallic state, and there is only one definite mineral known which contains it in quantity, namely, the sulfid, or greenockite, which is found in Renfrewshire, Scotland. This contains 77.7 per cent. of cadmium and 22.3 per cent. of sulfur.

The production of cadmium is confined to a very few localities in Belgium and England. It occurs in zinc blende to the extent of about 0.2 per cent. In the calcination of the blende the cadmium, volatilizing at a lower temperature than the zinc, passes off before the latter assumes the form of vapor. The oxid of cadmium is collected in condensing-tubes, and is subsequently reduced to the metallic state by heating with carbon.

Cadmium is a white metal with a slight bluish tinge. It is somewhat lighter in color than zinc or lead. It is susceptible of a high polish. It has the fibrous fracture characteristic of soft, tough metals. It differs from zinc in its crystalline form, that of cadmium being the octahedral, while that of zinc is rhombohedral. It is harder than tin, but not so hard as zinc, and is sufficiently malleable to admit of rolling into thin sheets. Its specific gravity after fusion is 8.6. Its electric conductivity is 22.10,—somewhat lower than

that of zinc. It melts at a temperature below redness ( $315^{\circ}$  to  $320^{\circ}$  C.).

Cadmium has been used in the formation of dental alloys, but its employment as a constituent in amalgams is now so generally condemned that it is seldom used for that purpose.

Probably the best test for cadmium is the color afforded when it is volatilized and oxidized under the blow-pipe flame. This is a reddish-brown, zinc under the same conditions giving a deposit which is a bright yellow while hot, becoming white on cooling. It may also be detected by precipitation from an acid solution as a yellow sulfid, and may in this way be distinguished from zinc, as zinc sulfid does not separate except from neutral or alkaline solutions.

In quantitative analysis cadmium is always estimated as oxid, being separated from solution as carbonate by precipitation with carbonate of sodium, which is converted into oxid by calcination. It may also be separated from its solution in acids by means of zinc, which precipitates it in a dendritic form, like the well-known lead tree.

## CHAPTER XVIII.

### ALUMINUM.

ATOMIC WEIGHT, 27.4. SYMBOL, AL.

*OCCURRENCE.*—Aluminum is never found in the metallic state. Of all the metals the sources of alumina are the most numerous and abundant. Its chief combinations are with silicon and other bases. These substances undergoing atmospheric changes form clays and soils, which under the influence of heat and moisture become fruitful. It would seem that its presence is not necessary to the maintenance of animal or vegetable life, since no traces of it have been found in either. Some of the compounds of aluminum are quite unattractive, but there are a number possessing great hardness and extraordinary beauty. The following with their formulæ are a few examples of the latter :

Ruby*	$\text{Al}_2\text{O}_3.$
Sapphire	$\text{Al}_2\text{O}_3.$
Garnet	$(\text{Ca Mg Fe Mn})_3\text{Al}_2\text{Si}_3\text{O}_{12}.$
Cyanite	$\text{Al}_2\text{SiO}_5.$

As early as 1760 Guytori de Morveau called the substance obtained by calcining alum alumina. Lavoisier, sixteen years later, suggested the existence of metallic bases of the earths and alkalies, and alumina was thought to be an oxid of a metal which was<sup>o</sup> called aluminium ; and thus it was named long before it was isolated.

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\*Corundum, the ruby, and the sapphire have the same chemical formula,  $\text{Al}_2\text{O}_3.$



In 1807 Sir Humphry Davy tried to decompose alumina by means of an electric current, and again to reduce the metal by vapor of potassium, in both of which experiments he failed.

In 1827 Wöhler isolated the metal by decomposing aluminium chlorid by potassium. The metal first isolated by Wöhler was a gray powder, taking under the burnisher the appearance of a highly polished metal. Later, in 1845, Wöhler obtained the metal in small malleable globules by making a vapor of aluminum pass over potassium placed in platinum vessels, and from these specimens he was able to determine the properties of the metal with some degree of accuracy.

The credit of the reduction of aluminum in a state of purity and the determination of its true properties belongs to H. St. Clair Deville, who in 1854 brought it from the rank of a mere laboratory curiosity to that of the useful metals.

In 1854 the Emperor Napoleon III, in the hope that aluminum might be used in the construction of armor and helmets for the French cuirassiers, authorized experiments on a large scale to be carried on at his own expense. In 1855 the Emperor put the necessary funds at the disposal of Deville, whose experiments were continued for four months, the result being that in August of the same year aluminum was placed on the market in Paris at 300 francs a kilo.

The first article known to have been made of aluminum was a baby-rattle for the infant Prince Imperial, for which purpose it was well fitted on account of its sonorousness; but application of the metal to the manufacture of cuirasses and helmets was decided to be impracticable, and the idea was abandoned.

*Reduction of Aluminum.*—A mixture of the double chlorid of aluminum and sodium, or the double fluorid of aluminum and sodium (cryolite), is heated to redness with the metal sodium, when energetic chemical action takes place, during which chlorid of sodium is formed and the metal aluminum separated.

Aluminum may be separated by electrolysis. The electric current from a ten-cell battery, provided with carbon poles, is passed through the fused salt. The metal appears at the negative pole in large globules.

In 1882 the cost of aluminum was materially lessened by inventions of Webster, of Birmingham, England. This inventor's method of producing the metal consisted in reducing sodium compounds in cast-iron pots from a fused bath of caustic soda. By this means the yield of sodium is much greater than by the method of Deville, while the temperature required in the operation is considerably less.

In 1859 Mr. Chas. M. Hall, of Ohio, obtained letters-patent for an electrolytic method which is superior to any that preceded it. The principal feature of this process is the electric decomposition of alumina suspended or dissolved in a fused bath of the salts of aluminum, the current reducing the alumina without affecting its solvent. Mr. Hall has succeeded in producing the metal aluminum as an article of commerce at \$2.00 per pound.

Aluminum is nearly the color of new zinc. It is very malleable and ductile, and admits of rolling into thin sheets, or it may be drawn into fine wire. It is highly sonorous, and has the power of conducting heat and electricity in about the same degree as silver. It is only two and a half times heavier than water (four

times lighter than silver). Its specific gravity is 2.56, and it melts at a red heat.

Aluminum does not oxidize in air, and is not attacked by sulfur compounds. It is not attacked by strong nitric acid, and is insoluble in dilute sulfuric acid, but it may be readily dissolved in either dilute or strong hydrochloric acid, which is its true solvent. The metal is easily dissolved in solutions of caustic potash or soda.

As the result of the invention of the electrical furnace of the Messrs. Cowles, of Cleveland, Ohio, aluminum bronze is made directly from corundum ( $\text{Al}_2\text{O}_3$ ). Twenty-five pounds of the crushed ore is mixed with about fifty pounds of copper and twelve pounds of a mixture of charcoal and electric-light carbon, and placed in a rectangular box of fire-brick, lined with limed charcoal to prevent loss of heat by radiation and to protect the fire-brick from disintegration. The charge is surrounded on all sides by a layer of charcoal to prevent the alloy from being contaminated with calcium from reduction of the lime present. The cast-iron slab forming the cover of the furnace is then securely luted on, and the current from a powerful dynamo-electric machine is passed into the furnace by means of two large electric-light carbons which pass through the ends of the furnace and into its contents. It requires about five hours of exposure to the intense heat afforded by the electric current to reduce the aluminum from its ore. When the furnace has cooled sufficiently the product of the reduction will be found to consist of about fifty pounds of a copper alloy containing from 15 to 35 per cent. of aluminum, which may be brought to the usual 10 per cent.

standard of aluminum bronze by remelting it with the proper proportion of copper.

The reaction which takes place in the process, which is aided by the intense heat of the electric current, is probably as follows: The carbon unites with the oxygen from the corundum, forming carbon monoxid; a small percentage of the aluminum remains free, mixed in small particles with the charcoal, while the greater portion unites with the copper to form the alloy. Nearly all the oxid is reduced and the charcoal is changed to graphite. Some of the aluminum unites with carbon to form the carbid of aluminum. The fusing-point of 10 per cent. aluminum bronze is somewhat below that of pure gold.

Aluminum may be melted in an ordinary clay crucible. No flux need be used. Borax is not only useless but is actually hurtful, as aluminum readily attacks the glasses. Biederman\* recommends dipping the scraps which are to be melted together in benzine before putting in the crucible. Should any of them be contaminated with solder it may be removed by immersing in nitric acid, which does not act upon the aluminum.

*Annealing.*—Aluminum may be softened by heating to redness and chilling suddenly by dropping into water. Richards recommends rubbing the piece to be annealed with tallow and then heating until the fat is carbonized, when at the moment the last trace of black disappears from the metal it may be dropped into water.

*Alloys.*—Aluminum forms alloys with nearly all the metals. That with copper† is the most important,

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\*“Aluminum: Its Properties, Metallurgy, and Alloys.” Richards.

†Aluminum bronze—alloy of copper with five per cent. of aluminum.

and presents a closer resemblance to gold than, perhaps, any other alloy. It is used for articles of jewelry, for mountings of astronomical instruments, and for making balance-beams.

German dentists are now using aluminum bronze as a base for artificial dentures. Professor Sauer, in a paper on the application of this alloy to dental purposes, says, "That in the proportion of Cu. 900 to Al. 100 it oxidizes but superficially in the mouth, and is as strong and resistant to attrition as 18-carat gold; it may be swaged as easily as 20-carat gold, but it must be annealed frequently, and it is necessary to carry the heating almost to whiteness, for if the bronze be merely heated until it assumes a dark-red color it remains as hard as before." He also gives the point of fusion of the alloy as above that of 18-carat gold, so that 14- or 18-carat gold solder alloyed with copper may be used upon it without difficulty. Although the alloy is highly recommended by many German dentists, the author does not hesitate to express the opinion that it will not find favor in this country.

The following solders are well adapted to aluminum bronze :

1. Hard Solder for 10 per cent. Aluminum Bronze.	
Gold	88.88 per cent.
Silver	4.68 "
Copper	6.44 "
	<hr/>
	100.00
II. Medium Hard Solder for 10 per cent. Aluminum Bronze.	
Gold	54.40 per cent.
Silver	27.00 "
Copper	18.00 "
	<hr/>
	100.00

## III. Soft Solder for Aluminum Bronze.

Copper	70 per cent.	} Brass	14	30 per cent.
Tin	30 "		Gold	14.30 "
			Silver	57.10 "
			Copper	14.30 "
			<hr/>	
			100.00	

Aluminum with tin and zinc forms a brittle alloy, and with silver it yields a hard, though workable compound. Aluminum amalgamates with mercury by the assistance of heat, and at the boiling-point of mercury the solution is very rapid.

Aluminum may be made to unite with mercury by the intervention of a solution of caustic potash or soda. If the surface of the metal be well cleaned, or moistened with the alkaline solution, it is immediately melted by the mercury, but the affinity of the aluminum for oxygen is greatly increased by the state of fine division, so that the amalgam when exposed to the air soon becomes covered with a white excrescence, which Watts found to be pure alumina.

Aluminum is employed in the manufacture of very small weights, such as the milligram of the metric system,—a use to which, in consequence of its exceedingly low specific gravity, it is particularly well adapted.

Its lightness, strength, and resistance to oxygen and the sulfur compounds, are properties which would seem to point to this metal as a suitable substance as a base for artificial teeth. The readiness, however, with which it is attacked by alkaline solutions renders it unfit for use in the construction of a permanent artificial denture.

Aluminum, notwithstanding its extreme lightness, may be cast with great exactness. The late Dr. J. B. Bean, who patented a process for casting aluminum, succeeded in producing castings of exquisite fineness. Indeed, it may be stated that Bean succeeded in overcoming all the physical difficulties encountered in the effort to render aluminum available in prosthetic dentistry, but its susceptibility to the action of alkaline solutions finally compelled him to abandon it.

Dr. C. C. Carroll, of Meadville, Pa., has devised a means of casting aluminum, which while much simpler than the method of Dr. Bean, affords results equally good. The metal is melted in a plumbago crucible having the form of a thick-walled cylinder closed at one end which serves as a bottom. A channel is formed within the wall of the crucible, one orifice of which terminates within at the side close to the bottom. Starting from the orifice, the channel rises in the crucible wall near the top, making a sharp return upon itself, and descends in a parallel course after the manner of a syphon, and makes its exit at the base and near the side of the crucible. Here it terminates in an iron nipple that fits into a corresponding socket in the gate-way of the molding-flask. A cylindrical plug of soapstone which fits the open mouth of the crucible is provided with a central tube of brass, to the free end of which is connected by a short length of rubber tubing a large rubber bulb. When the metal has been brought to a state of fusion the crucible is connected by means of the iron nipple at its base with the gate-way of the flask, which has been previously heated to redness, and the soapstone plug is

inserted in the mouth of the crucible. Compression of the air at this point by means of the rubber bulb forces the fluid metal out of the crucible through the syphon-like channel into the mold, filling the most minute lines and affording an exceedingly fine casting. Carroll makes the somewhat extraordinary statement that he has found a means of controlling the contraction of the metal, together with its tendency to disintegrate from exposure to the fluids\* of the mouth, by the admixture of other metals.

Richards, in his valuable work on aluminum, states that to overcome the difficulties of contraction and corrosion by the fluids of the mouth Dr. Carroll adds "a little copper, which, he says, decreases the contraction, while the addition of some platinum and gold renders it unalterable in the mouth."

Aluminum may be cast upon plain teeth with comparative safety, provided the metal is prevented from overlapping the necks of the teeth. But when gum teeth are employed, either single or in sections, their fracture is almost certain to follow the contraction incident to the cooling of the metal. Specimens of Dr. Carroll's work have fully proved this, and it was the one difficulty which finally defeated Dr. Bean's efforts by compelling him to cast his plate separate from the teeth. For, if it had been practicable to cast the metal directly upon block teeth without danger of fracture, the denture would have lasted for at least six or eight years; but the necessity of attaching the teeth to the plate by another metal so hastened disintegration that a few months only were necessary to render the piece useless.

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\* Demonstration before dental class, University of Pennsylvania.



There are two methods which have been employed in the construction of artificial dentures of this metal. The one most frequently resorted to consists in merely swaging a plate in the ordinary way. A number of countersunk holes are then made along the part covering the top of the alveolar ridge, as a means of fastening the teeth, which are attached with rubber or celluloid. Sets of teeth made in this way have been known to do good service for eight or nine years, but they showed unmistakable evidence of the action of the oral fluids. In the second method the plate is cast, but disintegration in this case progresses with much greater rapidity. As the plate is cast separate from the teeth, and the latter are afterward attached by means of tin or an alloy of tin and aluminum, it is probable that the galvanic action incident to the presence of the two metals greatly hastens solution of the plate.

For some time the difficulty of soldering aluminum prevented the metal from being applied to useful purposes. The solder recommended for general use in the manufacture of articles of ornamentation is composed of copper, four parts; aluminum, six parts; zinc, ninety parts. The use of this requires some skill and experience. At the moment of fusion small aluminum tools are used, the friction of which is necessary to induce adhesion. Borax cannot be employed as a flux, as it is liable to attack the metal and prevent union.

Another method of uniting two pieces of aluminum with ordinary solder in conjunction with silver chlorid as a flux has recently been recommended by F. J. Page and H. A. Anderson, of Waterbury, Conn. The finely

powdered fused silver chlorid is spread along the lines of junction, and the solder is melted with a blow-pipe or other device. The union thus obtained is said to be perfectly strong and reliable.\*

The following alloys are also used as solders in unalloyed aluminum articles of jewelry :

	I.	II.	III.	IV.
Zinc .	80	85	88	92
Aluminum	20	15	12	8

In soldering with these alloys a mixture is used as a flux consisting of three parts copaiba balsam, one part Venetian turpentine, and a few drops of lemon-juice. The soldering-iron is dipped into the mixture.

Mr. Wm. Frishmuth, of Philadelphia, recommends the following solders for aluminum, with vaselin as the flux :

Soft Solder.

Pure Block Tin	from 99 to 90 parts.
Bismuth	“ 1 “ 10 “

Hard Solder.

Pure Block Tin .	from 98 to 90 parts.
Bismuth	“ 1 “ 5 “
Aluminum .	“ 1 “ 5 “

Schlosser† recommends two solders containing aluminum as especially suitable for dental laboratory use :

Platinum-Aluminum Solder.

Gold	30 parts.
Platinum	1 “
Silver	20 “
Aluminum	100 “

\* Chemical News, iv, 81.

† Richards.

## Gold-Aluminum Solder.

Gold	50 parts.
Silver	10 “
Copper	10 “
Aluminum	20 “

O. M. Thowless has patented the following solder for aluminum, and method of applying it :

Tin	55 parts.
Zinc	23 “
Silver	5 “
Aluminum	2 “

The silver and aluminum are first melted together, the tin and zinc are then added in the order named. The surfaces to be soldered are immersed in dilute caustic alkali or a cyanid solution, and then washed and dried. They are next heated over a spirit-lamp, coated with the solder, and clamped together ; small pieces of the solder being placed at the points of union, the whole is then heated to the melting-point. No flux is used.

The only oxid of this metal is alumina ( $Al_2O_3$ ). It is prepared by mixing a solution of alum with excess of ammonia. The resulting precipitate (aluminum hydrate) is of a bulky, gelatinous character, and requires to be calcined at a high temperature ; after which it may be described as a perfectly white powder, soluble in caustic potassa or soda, and not readily acted upon by acids. Corundum and emery are nearly pure alumina. The ruby and sapphire are also transparent varieties of alumina in a crystalline state, their brilliant colors being due to oxid of chromium.

The only known sources of corundum until 1869 were a few rivers in India, where it occurred in crys-

tals having the form of the double six-sided cone. Its cost at that time was from twelve to twenty-five cents a pound. Since that date, however, it has been discovered in inexhaustible quantities in Georgia, North Carolina, and Pennsylvania. At present it can be bought at the mines at \$10 per ton.

For the discrimination of the salts of aluminum, see any of the recent works on chemistry.

## CHAPTER XIX.

### LEAD.

ATOMIC WEIGHT, 207. SYMBOL, Pb (PLUMBUM).

THE reduction of lead is effected in a reverberatory furnace, in which the broken lead ore (galena) is roasted at a dull-red heat, by which means the sulfid becomes oxidized and converted into sulfate. At this stage of the operation the contents of the furnace are thoroughly mixed and the temperature raised, which causes the sulfid and sulfate to react upon each other, producing sulfurous oxid and metallic lead.

Lead is the softest metal in common use, and may be said to be the least tenacious. In fusibility it also surpasses all other metals commonly employed in the metallic state except tin, the fusing-point of lead being  $617^{\circ} \text{F.} = 325^{\circ} \text{C.}$  It is quite malleable and ductile, and will admit of being rolled into thin sheets or foil, in which form it was at one time much used in filling teeth. Its chief use in the dental laboratory consists in the formation of counter-dies.

*Alloys.*—Lead unites with tin in all proportions, the resulting alloys being more tenacious and fusible than either constituent. By the addition of bismuth the fusing-point is reduced below the boiling-point of water.

Lead amalgamates readily with mercury, condensation accompanying the union. The noble metals are all rendered brittle and unworkable by the pres-

ence of lead. There are some properties peculiar to alloys of lead and silver which are turned to advantage in the separation of silver from lead when it occurs as a native alloy. Lead combined with a considerable quantity of silver will remain fluid at a lower temperature than other specimens containing a smaller percentage, thus affording an opportunity for the poorer lead to crystallize, when it is ladled out.\*

The smallest proportion of lead in gold will greatly impair the ductility of the latter. Makins states that "Hatchett found that  $\frac{1}{10\frac{1}{2}0}$  of lead destroyed the coining qualities of gold." Gold reduced to standard fineness by lead is light-yellow in color, and quite brittle. The contents of the dentist's gold-drawer are always liable to contamination by small pieces of lead, the latter being much used in the form of thin sheets in the making of patterns by which the gold or silver plate is cut. As the working qualities of the precious metals are seriously impaired by its presence, means should be instituted to insure its complete removal. This may be accomplished by cupellation, or by melting the gold or silver in a crucible, and adding nitrate of potassium when the point of complete fusion has been reached.

Lead and platinum, like tin and platinum, appear to possess considerable affinity for each other, and an alloy of the two can be formed at a comparatively low temperature.

An alloy of lead and platinum is very hard and brittle. With palladium also lead forms a very hard and brittle alloy.

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\* See chapter on "Silver."

The most valuable alloys of lead are those which it forms with tin, antimony, and bismuth, constituting solders, pewter, type-metal, etc.

For the discrimination of lead, the student is referred to Fownes's or other standard works on chemistry.

## CHAPTER XX.

### TIN.

ATOMIC WEIGHT, 118. SYMBOL, SN (STANNUM).

THE metal tin has been known for probably three thousand years. It is found in all parts of the world, chiefly as oxid. In reducing the ore it is first powdered and roasted to free it of sulfur and arsenic. It is then exposed to a high temperature with charcoal, and the metal is thus liberated.

Pure tin is white in color, and is perfectly soft and malleable. It has a density of 7.3, and its fusing-point is 458.6° F. (237° C.). It is but slightly acted upon by air, but when heated much above its melting-point it oxidizes freely, and is converted into a yellowish-white powder,—the well-known polishing-putty. The action of nitric acid upon tin is to convert it into a white hydrated dioxid. It is dissolved by hydrochloric acid, assisted by heat, and forms stannous chlorid. Nitro-hydrochloric acid acts upon tin with much energy, converting it into stannic chlorid.

*Alloys.*—Tin is readily dissolved in mercury (see page 50). With silver it forms a malleable alloy, which is considerably harder than tin. The late Dr. Bean used tin alloyed with a small percentage of silver for lower sets, which he cast directly upon the teeth after the ordinary cheoplastic method.

Alloys of tin and silver, in which the former is slightly in excess, are much used as amalgam alloys.



Tin 10, silver 8, gold 1, is also frequently employed in filling teeth ; and tin 10, silver 8, gold 1, copper 1, has, according to Fletcher, been largely used as "gold and platinum" amalgam. It is stated that from 5 to 7 per cent. of copper has the property of replacing platinum in amalgams, conferring the quick-setting quality claimed for platinum.\*

Dr. G. F. Reese has formed an alloy for a base for artificial dentures, composed of 20 parts of tin, 1 of gold, and 2 of silver.† This is cast directly upon the teeth, the process being similar to the cheoplastic method.

The alloys which have been used in the cheoplastic process are chiefly composed of tin, silver, bismuth, and, in some instances, cadmium and antimony.

According to Makins, gold and tin form a malleable alloy,‡ and gold reduced to standard by pure tin retains its malleability.

Tin and platinum in equal proportions afford a hard and quite brittle alloy, fusible at a comparatively low temperature. When it is remembered that the fusing-points of these metals almost represent extremes of temperature, it would seem that their union must be attended with difficulty, but, as has already been stated,|| it is probable that some affinity exists between the two, as platinum is readily dissolved by and alloys with the fused tin.

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\* T. Fletcher.

† Alloys and Amalgams Chemically Considered," J. Morgan Howe, M.D.

‡ A precipitated alloy of gold and tin, having the form of a black powder, may be formed by acting upon a concentrated solution of trichlorid of gold with stannous chlorid.

|| See chapter on "Alloys."

With palladium tin is said to form a brittle alloy.

With lead tin forms the chief part in the alloys used for soft-soldering, and in the compounds known as pewter and Britannia-metal. Tin solders are composed of two parts of tin to one of lead. Pewter consists of four parts of tin to one of lead, while Britannia-metal is formed by the addition of small quantities of antimony and copper.

Alloys of tin and lead are harder and tougher than either metal singly, and they are more fusible than the mean of their constituents. The addition of bismuth to such an alloy lowers the melting-point to a remarkable degree, and the fusing-point is still further reduced by the addition of cadmium. Thus, an alloy composed of 15 parts of bismuth, 8 of lead, 4 of tin, and 3 of cadmium, fuses at  $145^{\circ}$  F. =  $63^{\circ}$  C.

Dr. C. M. Richmond used a fusible alloy in crown- and bridge-work which he states is as hard as zinc, and can be melted at  $150^{\circ}$  F., and poured into a plaster impression without generating steam. The formula of this alloy is as follows :

Tin	20 parts by weight.
Lead .	19 " " "
Cadmium	13 " " "
Bismuth	48 " " "

The following fusible-metal alloys are also suitable for the purpose :

Tin.	Lead.	Bismuth.	Melting-point of Alloy. Fahr.
1	2	2	$236^{\circ}$
5	3	3	$202^{\circ}$
3	5	8	$197^{\circ}$

Dr. George W. Melotte, of Ithaca, N. Y., to

whom is due the credit of having introduced the use of fusible metal and the compound called "moldine" into bridge-work, uses an alloy of—

Tin,	5,
Lead,	3,
Bismuth,	8.

Moldine, of which Melotte forms his matrix for casting, is a compound of potter's clay and glycerin.

The alloy known as "Wood's metal," occasionally employed by dentists in replacing teeth on vulcanite plates, is composed of 7 parts of bismuth, 6 of lead, and 1 of cadmium, and fuses at  $180^{\circ}$  F. =  $82^{\circ}$  C., a point much below the boiling-point of water. In replacing a broken tooth by means of Wood's metal the usual dovetail is cut in the rubber plate with a fine saw, the tooth is fitted to its place, and the fusible alloy is packed in with a spatula heated in a spirit-lamp.

Lead 75, tin 5, and antimony 20 parts, is the composition of the best form of type-metal.

With copper tin affords a number of very useful alloys. Bell-metal is formed of 78 parts of copper to 2 of tin. Gun-metal is formed of 90 per cent. of copper to 10 per cent. of tin. Speculum-metal is formed of 6 parts of copper, 3 of tin, and 1 of arsenic.

Babbitt-metal, named after Isaac Babbitt, of Boston, Mass., is an alloy consisting of 9 parts tin, 10 parts copper, used for journal boxes (*vide* patent 1839). Many modifications have since been made in this alloy, but the term is still applied to any white alloy employed in the construction of bearings, to distinguish it from the "bronzes" and "brasses."

Mr. Fletcher recommends an alloy of copper 4

pounds, Banca tin 96 pounds, Regulus antimony 8 pounds. This alloy is said to be nearly as hard as zinc, while its shrinkage is much less. These quantities, together with the low temperature at which it fuses, entitle it to a place in the dental laboratory for the preparation of dies and counter-dies.

Dr. L. P. Haskell recommends the formula, tin 72.72, copper 9.09, antimony 18.18.

Bronze is an alloy of copper and tin, and sometimes zinc. It is affected by changes of temperature in a manner precisely the reverse of that in which steel is affected, becoming soft and malleable when quickly cooled, and hard and brittle when allowed to cool slowly. The art of making bronze was practiced before any knowledge of the working of iron existed, and it was used at a very early period in the manufacture of weapons.

Commercial tin is liable to contain minute quantities of lead, iron, copper, arsenic, antimony, bismuth, etc. Pure tin may be precipitated in crystals by the feeble galvanic current excited by immersing a plate of tin in a strong solution of stannous chlorid. Water is carefully poured on so as not to disturb the layer of tin solution. The pure metal will be deposited on the bar of tin at the point of junction of the water and the metallic solution.

Perfectly pure tin may also be obtained by dissolving commercial tin in hydrochloric acid, by which it is converted into stannous chlorid. After filtering, this solution is evaporated to a small bulk, and treated with nitric acid, which instantly converts the stannous chlorid into stannic oxid. This is thoroughly washed and dried, and exposed to red heat in a cruci-

ble with charcoal. A button of pure tin will be found at the bottom of the crucible.

Pure tin in the form of foil is frequently used in filling teeth, for which purpose it doubtless ranks next to gold. Tin foil is also employed in connection with non-cohesive gold in filling approximal surfaces of cavities in bicuspid and molars. Two sheets of foil, one of gold and the other of tin, are placed together and made into mats or cylinders. These are carefully packed against the cervical margins of the cavity. The frequent failure of ordinary gold fillings at this point has led some practitioners to entertain the theory that between the tooth-substance and the gold there is galvanic action, to which the lime-salts of the tooth yield, and that by the combination of two metals, whether tin and gold or amalgam and gold, the galvanic action is confined to the metals, the tooth-substance being thus protected.

The appearance of a filling formed of tin and gold would seem to confirm this theory, as it soon becomes dark in color, and presents a surface resembling amalgam, but it effectually protects the margins from decay.\*

Tin having but slight affinity for sulfur, is largely used in the formation of models in the construction of vulcanite dentures, and tin foil forms the best coating for plaster casts in the vulcanizing process.

The manufacturers of miscellaneous rubber articles do not use plaster in forming the matrix in which the rubber is packed before vulcanizing; having long since discovered that contact with plaster lessens the

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\* Prof. James Truman, Report of Proceedings of Odontological Society of Pennsylvania, November, 1881.

toughness and elasticity of the indurated rubber, they therefore form every matrix of sheet tin, which is placed in a suitable iron box and covered tightly with dry powdered soapstone (steatite).

Dr. J. S. Campbell, who introduced the vulcanizer known as the "New Mode Heater," described a means whereby all parts of the matrix contained in the flask in constructing rubber dentures could be covered by sheet tin, so that after vulcanizing and the removal of the sheet tin or foil the surface of the rubber would be found to be smooth and highly polished, and if the "waxing up" had been carefully done, little or no filing and scraping were needed. The method demonstrated by Dr. Campbell possessed precision and saved labor, and it is to be regretted that it was not generally adopted by mechanical dentists, who have not improved to any extent upon the slovenly methods employed in 1858, when indurated rubber was first employed in dental practice.

When tin foil is used as a coating for plaster casts in rubber work, the foil may be removed with the fingernail if the surface of the plaster model was smooth and hard, and this condition of the plaster surface can be obtained by using nothing as a coating for the plaster impression but sandarac varnish, and carefully avoiding the use of oil or solutions of soap as a means of separating the impression from the model. If, however, in consequence of the roughened surface of the plaster cast the tin foil adheres so tenaciously that it cannot be removed except by means of a solvent, hydrochloric acid is the only one that will accomplish that end without injury to the rubber. Both nitric and nitro-hydrochloric acids should be avoided, as

they attack indurated rubber with more or less energy.

Lower vulcanite dentures may be loaded with tin to give them additional weight, and by lessening the quantity of rubber prevent the occurrence of porosity during the process of vulcanizing.

*Solvents.*—Tin is readily dissolved by either of the three mineral acids. Sulfuric acid converts it into stannic sulfate. Tin dissolved in hydrochloric acid forms stannous chlorid. By the action of dilute nitric acid tin is not dissolved, but is converted into stannic oxid, which settles to the bottom of the vessel as a white powder. This, when rendered anhydrous by heating to redness, affords the well-known polishing-powder called "polishing-putty."

*Chlorids.*—There are two chlorids of tin,—stannous chlorid or protochlorid of tin ( $\text{SnCl}_2$ ), and stannic chlorid or bichlorid of tin ( $\text{SnCl}_4$ ). Stannous chlorid is prepared by dissolving tin in hydrochloric acid, the action being assisted by gentle heat. Stannic chlorid is obtained by dissolving tin in nitro-hydrochloric acid (aqua regia). These two compounds of tin are employed in the preparation of purple of Cassius, in which process stannous chlorid is added to a mixture of stannic chlorid and trichlorid of gold (see page 149).

For other compounds of tin, see works on chemistry.

*Discrimination.*—Tin is detected before the blow-pipe by fusing the compound under examination on charcoal with sodium carbonate, when a bead of the metal is obtained. From a tin solution caustic potash and soda precipitate a white hydrate, soluble in excess. Ammonia affords a similar precipitate, not soluble in

excess. Hydrogen sulfid and ammonium sulfid throw down a dark-brown precipitate of monosulfid. Trichlorid of gold added to a dilute solution of stannous chlorid causes a purple precipitate (purple of Cassius).



## CHAPTER XXI.

### ELECTRO-METALLURGY.

THE origin of electro-metallurgy was undoubtedly due to the early experiments of Wollaston and Davy, while the credit of its development belongs to the late Professor Daniell, who devised the particular form of battery which bears his name. A Daniell cell consists of a copper vessel containing a saturated solution of sulfate of copper. In this is placed a porous cylinder containing dilute sulfuric acid. A rod of amalgamated zinc is immersed in the acid, and on the two metals being connected, electrical action is immediately set up, and the zinc, which forms the positive element, is dissolved, with formation of sulfate of zinc; the sulfate of copper is reduced, and the metallic copper is deposited upon the surface of the copper vessel, which forms the negative element of the combination. It was observed that the copper thus deposited took the exact shape of the surface on which it was thrown, presenting a faithful counterpart of the slightest indentation or irregularity. De la Rue called attention to this fact in a paper published in 1836, but no practical application was made of it until 1839, when Professor Jacobi, of St. Petersburg, published his discovery of a means of producing copies of engraved copper plates by the agency of electricity.

In 1840 Mr. Murray announced that an electro-deposit of metal could be formed upon almost any

material, provided its surface was rendered a conductor of electricity by a thin coating of graphite (black lead). Instead of copying the object in a metallic medium, it is only necessary to take a cast in plaster of Paris, wax, gutta-percha, or any convenient material, and then to coat the surface with finely-powdered graphite applied with a camel's-hair pencil.

The Gramme machine, a modification of the magneto-electric apparatus, consists of a ring of soft iron carrying a number of coils of insulated copper wire, caused to rotate between the poles of a fixed horse-shoe magnet. The currents induced in the coils are collected by two metallic disks, whence they may be drawn off for use in electro-deposition. The core being circular, the magnetization proceeds continuously, affording a uniform current. Both poles of the magnet are used, producing simultaneously two opposite continuous currents. These and similar sources of electricity enable the electro-metallurgist to deposit a metal upon a matrix or to coat one metal with another.

The art of electro-metallurgy is divided into two branches, electrotypy and electro-plating. In the former the reduced metal is separated from the mold on which it is deposited, forming a distinct work of art, while in the latter the deposited metal forms an inseparable part of the plated object. Electrotypy is employed in producing copper duplicates of engravings on wood and of any kind of type-matter for printers' use. A cast of the object is first taken in wax or gutta-percha, and the surface of this mold is brushed over with black-lead, and it is then, by means of a wire, suspended in a bath of sulfate of copper

connected with a battery. Since the introduction of dynamic electricity, perfect copies may be produced in an hour or two, and the deposited metal made thick enough to stand any reasonable amount of wear.

Electro-plating, by which silver is deposited on the surfaces of objects of copper, brass, or German-silver, was introduced soon after the discovery of the art of electro-metallurgy. The article to be plated must first be thoroughly cleansed by immersing it in a hot solution of caustic potash, and also by means of the "scratch-brush," and sometimes by "pickling" it in a bath of nitric and other acids. The surface is then given a thin film of mercury, by washing the article with a solution of mercuric nitrate. This is called "quicking." The article is then rinsed with water and transferred to the silver bath, which consists of a solution of cyanid of silver in cyanid of potassium,—a very poisonous compound. Plates of silver are suspended from a rectangular frame connected with the positive pole, while the articles to be plated are suspended by wires attached to the negative pole. The quantity of silver to be deposited depends upon the requirements of the case. One ounce of silver per square foot forms for ordinary purposes a sufficiently heavy coating.

Electro-gilding is effected by means similar to those employed in electro-silvering. The solution employed is generally the double cyanid of gold and potassium, and it is used hot, the temperature ranging from 130° F. to 212° F., according to the ideas of the operator.

Nickel-plating was first introduced in 1869, by Dr. Isaac Adams, of Boston, who patented a process for

depositing nickel from solutions of double salts of sulfate of nickel and ammonium.

Iron may also be deposited from the double sulfate of iron and ammonium. Practical application is now made of this discovery, and engraved copper plates are found to be much more durable when faced with electro-deposited iron. Plates for printing bank-notes are sometimes treated in this way.

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