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THE
CHEMIST

APPLETON

THE

METALS OF THE CHEMIST

AN

ELEMENTARY TEXT-BOOK

FOR

SCHOOLS AND COLLEGES.

BY

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PROFESSOR APPLETON'S CHEMICAL TEXT BOOKS.

The Chemistry of the Non-metals. An elementary text-book for schools and colleges. The subject matter is so divided that reference data are separated from descriptive text. Again the text is very carefully *classified*; the student soon becomes aware of the orderly arrangement of topics. The book has other valuable features; they will be recognized by teachers upon inspection.

The Metals of the Chemist. This is an elementary text-book for schools and colleges. It deals with all the recognized metals and with many of the most important applications of them.

The Carbon Compounds. An elementary organic chemistry. This book, with the two preceding, is intended to complete a brief course covering the entire field of *general* chemistry.

The Young Chemist. A book of chemical experiments for beginners in chemistry. This is designed for use in schools and colleges. It is composed almost entirely of experiments, those being chosen that may be performed with very simple apparatus. The book is arranged in a clear, systematic, and instructive manner.

Easy Experiments of Organic Chemistry. This book gives clear and distinct instructions for the performance of above 100 experiments of Organic Chemistry. Any teacher of chemistry or any intelligent pupil who will try, *exactly as described*, a few experiments, will be astonished at the ease and perfection with which results are obtained. The experiments require only simple apparatus, and they may be performed quickly.

Qualitative Analysis. A brief but thorough manual for laboratory use. It gives full explanations and many chemical equations. The processes of analysis are clearly stated, and the whole subject is handled in a manner that has been highly commended by a multitude of successful teachers of this branch.

Quantitative Analysis. A text-book for school and college laboratories. This volume possesses novel and striking merits, such as will make it worthy of the same decided approbation and large sale that have been awarded to the earlier books of this series. The treatment of the subject is such that the pupil gains an acquaintance with the best methods of determining all the principal elements, as well as with the most important type processes both of gravimetric and volumetric analysis.

First Report-book; for Chemical Experiments. A well-arranged memorandum book, with blank space to be filled by the pupil during the progress of his experiments. The making of a succinct report by the student is of great service in leading him to form the habit of taking written notes while the facts of the experiment are fresh in the mind. Moreover, it undoubtedly increases the powers of observation.

This Report-book is so constructed that it may be used with "The Young Chemist" or with any text-book on general chemistry.

Second Report-book; for Qualitative Analysis. It is so arranged that it may be used with Appleton's Qualitative Analysis.

Third Report-book; for Quantitative Analysis. It is so arranged that a student may preserve a statement of his work in this branch. Spaces are provided for the record of the weights of crucibles, etc., and a blank page is afforded for the computations necessary in each case.

Chemical Philosophy. This book deals with certain general principles of chemical science, such as the constitution of matter; atoms, molecules, and masses; the three states of matter and radiant matter; the change of state from one form of matter to another. It also presents such topics as Boyle's and Mariotte's law, Charles' law, and the other general laws of matter. It discusses from a chemical standpoint certain forms of energy, such as heat, light, electricity. It treats of the nature of chemical affinity; the chemical work of micro-organisms; the modes of chemical action; thermo-chemistry; and those attractions of substances which are partly physical and partly chemical. It also presents a full study of atomic weights; the methods leading to a first adoption of them, and then to the grounds sustaining certain numbers selected. The periodic system is of course discussed.

PREFACE.

This little volume is one of three text-books on *general or descriptive chemistry*, prepared by the same author, viz.:

I.— The Chemistry of the Non-metals. II.— The Metals of the Chemist (the present volume). III.— The Carbon Compounds (a short treatise on organic chemistry).

These three books are intended to represent a tolerably complete course for general, as distinguished from professional students. In each case, however, it is expected that the use of the works mentioned will be supplemented by lectures and by individual laboratory work by the pupil.

Brown University, Providence, R. I.
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THE METALS OF THE CHEMIST.

INTRODUCTION.

At the present time, chemists acknowledge the existence of about seventy-four elementary substances. About eighteen of these are classified as non-metals and about fifty-six as metals. Lists of the elements, both in the alphabetical order of their names, and in the order of their atomic weights, are presented on pp. 2 and 3.

The eighteen *non-metals* are mentioned below :

TABLE OF EIGHTEEN NON-METALS.

Monads	Dyads	Triads	Tetrads
hydrogen			
....		boron	
fluorine	oxygen	nitrogen	carbon
....	....	....	....
chlorine	sulphur	phosphorus	silicon
bromine	selenium	arsenic	
iodine	tellurium	antimony	

To this list must be added, argon and helium, as yet, unclassified. (Perhaps krypton, metargon, neon, and xenon should be included.)

TABLE OF 74 ELEMENTS (3 DOUBTFUL ONES ADDED)

IN ALPHABETICAL ORDER. O=16. (CHIEFLY F. W. CLARKE'S NUMBERS.)

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
Aluminium	Al	27.11	Metargon	Mt	40. ?
Antimony	Sb	120.43	Molybdenum	Mo	95.99
Argon	A	39.88?	Neodymium	Nd	140.80
Arsenic	As	75.01	Neon	Ne	19.2?
Barium	Ba	137.43	Nickel	Ni	58.69
Bismuth	Bi	208.11	(Niobium, see Columbium)		
Boron	B	10.95	Nitrogen	N	14.04
Bromine	Br	79.95	Osmium	Os	190.99
Cadmium	Cd	111.95	Oxygen	O	16.
Caesium	Cs	132.89	Palladium	Pd	106.36
Calcium	Ca	40.07	Phosphorus	P	31.02
Carbon	C	12.01	Platinum	Pt	194.89
Cerium	Ce	140.20	Potassium	K	39.11
Chlorine	Cl	35.45	Praseodymium	Pr	143.60
Chromium	Cr	52.14	Rhodium	Rh	103.01
Cobalt	Co	58.93	Rubidium	Rb	85.43
Columbium	Cb	93.73	Ruthenium	Ru	101.68
(or Niobium)			Samarium	Sm	150.26
Copper	Cu	63.60	Scandium	Sc	44.12
Erbium	E	166.32	Selenium	Se	79.02
Fluorine	F	19.06	Silicon	Si	28.40
Gadolinium	Gd	156.76	Silver	Ag	107.92
Gallium	Ga	69.91	Sodium	Na	23.05
Germanium	Ge	72.48	Strontium	Sr	87.61
Glucinum	Gl	9.08	Sulphur	S	32.07
(or Beryllium)			Tantalum	Ta	182.84
Gold	Au	197.23	Tellurium	Te	127.49
Helium	He	4.28?	Terbium	Tb	160.0
Hydrogen	H	1.008	Thallium	Tl	204.15
Indium	In	113.85	Thorium	Th	232.63
Iodine	I	126.85	Thulium	Tu	170.70
Iridium	Ir	193.12	Tin	Sn	119.05
Iron	Fe	56.02	Titanium	Ti	48.15
Krypton	Kr	80. ?	Tungsten	W	184.83
Lanthanum	La	138.64	Uranium	U	239.59
Lead	Pb	206.92	Vanadium	V	51.38
Lithium	Li	7.03	Ytterbium	Yb	173.19
Magnesium	Mg	24.28	Yttrium	Yt	89.02
Manganese	Mn	54.99	Zinc	Zn	65.41
Mercury	Hg	200.00	Zirconium	Zr	90.40

TABLE OF 74 ELEMENTS (3 DOUBTFUL ONES ADDED)

IN THE ORDER OF ATOMIC WEIGHTS. O = 16. (CHIEFLY F. W. CLARKE'S NUMBERS.)

Name.	Symbol.	Atomic Weight.
Hydrogen	H	1.008
Helium	He	4.28?
Lithium	Li	7.03
Glucinum (or Beryllium)	Gl	9.08
Boron	B	10.95
Carbon	C	12.01
Nitrogen	N	14.04
Oxygen	O	16.
Fluorine	F	19.06
Neon	Ne	19.2?
Sodium	Na	23.05
Magnesium	Mg	24.28
Aluminium	Al	27.11
Silicon	Si	28.40
Phosphorus	P	31.02
Sulphur	S	32.07
Chlorine	Cl	35.45
Potassium	K	39.11
Argon	A	39.88?
Calcium	Ca	40.07
Metargon	Mt	40.?
Scandium	Sc	44.12
Titanium	Ti	48.15
Vanadium	V	51.38
Chromium	Cr	52.14
Manganese	Mn	54.99
Iron	Fe	56.02
Nickel	Ni	58.69
Cobalt	Co	58.93
Copper	Cu	63.60
Zinc	Zn	65.41
Gallium	Ga	69.91
Germanium	Ge	72.48
Arsenic	As	75.01
Selenium	Se	79.02
Bromine	Br	79.95
Krypton	Kr	80.?
Rubidium	Rb	85.43
Strontium	Sr	87.61
Yttrium	Yt	89.02
Zirconium	Zr	90.40
Columbium (or Niobium)	Cb	93.73
Molybdenum	Mo	95.99
Ruthenium	Ru	101.68
Rhodium	Rh	103.01
Palladium	Pd	106.36
Silver	Ag	107.92
Cadmium	Cd	111.95
Indium	In	113.85
Tin	Sn	119.05
Antimony	Sb	120.43
Iodine	I	126.85
Tellurium	Te	127.49
Caesium	Cs	132.89
Barium	Ba	137.43
Lanthanum	La	138.64
Cerium	Ce	140.20
Neodymium	Nd	140.80
Praseodymium	Pr	143.60
Samarium	Sm	150.26
Gadolinium	Gd	156.76
Terbium	Tb	160.0
Erbium	E	166.32
Thulium	Tu	170.70
Ytterbium	Yb	173.19
Tantalum	Ta	182.84
Tungsten	W	184.83
Osmium	Os	190.99
Iridium	Ir	193.12
Platinum	Pt	194.89
Gold	Au	197.23
Mercury	Hg	200.00
Thallium	Tl	204.15
Lead	Pb	206.92
Bismuth	Bi	208.11
Thorium	Th	232.63
Uranium	U	239.59

The Metals.

An element is classified as a *metal* when it possesses a certain set of properties somewhat as stated below :

First. Mechanical properties. A metal is generally heavier than water ; it possesses hardness, malleability and ductility.

A few elementary substances, however, (notably lithium, sodium, potassium,) are lighter than water ; on the other hand they possess, in a very distinct way, the chemical characteristics of metals.

Second. Physical properties. A metal generally exists at ordinary temperatures in the solid condition (or at any rate by moderate withdrawal of heat it assumes the solid condition). It possesses metallic lustre. It possesses opacity. It is generally a good conductor of heat and of electricity.

Mercury and gallium are liquid at ordinary temperatures, but they are easily reduced to the solid form, and then they are malleable and ductile ; but they possess in a distinct degree the *chemical* properties of metals.

Third. Chemical properties. A metal generally has but feeble chemical affinity for hydrogen (with which a non-metal generally combines readily). It tends to displace and liberate hydrogen from compounds of the latter. It combines with oxygen and thus forms oxides which generally are basic anhydrides (while a non-metal generally combines with oxygen, and thus forms oxides which are acid anhydrides). A metal in combination (when in a liquid solution) is generally electro-positive to the electric current (while a non-metal, under similar conditions, is generally electro-negative).

It must be admitted that but few of the so-called metals possess, in a high degree, all the properties just enumerated. A few elementary substances possess characteristics such that they are as much allied to the non-metals as to the metals. Thus, antimony is classified by some chemists as a metal, and tin is sometimes classified as a non-metal. If, then, all the elements are arranged in a series — commencing with the most distinct non-metal at one end and ending with the most distinct metal at the other end — some of the intermediate elements are found to possess physical and chemical properties such that they may be called metals or non-metals at the choice of the chemist.

Distribution of Metals in the Earth.

Quantitatively. — The percentage amounts of the elementary substances in our planet is a subject which has recently received a critical investigation by Prof. F. W. Clarke. He gives first the following tables of the percentage composition of the terrestrial globe in general :

	Density of crust assumed, 2.5.	Density of crust assumed, 2.7.
Atmosphere,	0.03 per cent.	0.03 per cent.
Ocean,	7.08	6.58
Solid crust,	92.89	93.39
	——	——
	100.00	100.00

Next he offers the following tables of elementary elements in detail :

Element.	Solid crust, 93 per cent.		Ocean, 7 per cent.	Mean, including air.	
Oxygen,	47.29		85.79	49.98	
Silicon,	27.21		....	25.30	
	——	74.50		——	75.28
Aluminium,	7.81		....	7.26	
Iron,	5.46		....	5.08	
Calcium,	3.77		0.05	3.51	
Magnesium	2.68		0.14	2.50	
Sodium,	2.36		1.14	2.28	
Potassium,	2.40		0.04	2.23	
	——	24.48		——	22.86
Hydrogen,	0.21		10.67	0.94	
Titanium,	0.33		....	0.30	
Carbon,	0.22		0.002	0.21	
Chlorine,	0.01		2.27	0.15	
Bromine,	....		0.008		
Phosphorus,	0.10		....	0.09	
Manganese,	0.08		....	0.07	
Sulphur,	0.03+		0.09	0.04+	
Barium,	0.03		....	0.03	
Nitrogen,	....		....	0.02	
Chromium,	0.01		....	0.01	
	——	1.02		——	1.86
55 others,	....	....	....	....	....
	100.00	100.00	100.00	100.00	100.00

From this table it appears 1st, that only six of the *metals* exist in the earth in quantities above 1 per cent. for each ; 2d, that only four of the *metals* exist in quantities between .01 per cent. and 1 per cent. ; 3d, that the *aggregate quantity of all the other forty-six metals* (plus that of nine non-metals) is less than .01 per cent.

It should be remembered that most of the metals (even those existing in very small quantities, like gold and lithium,) are very widely diffused in the material of the earth; in some cases (as in case of mercury) there is a tendency to localization of the substance. But localization is not as common as wide distribution.

Prof. Clarke adds the following interesting considerations: "The mean density of the earth, 5.5 to 5.6, is more than double that of the rocky crust, and the difference may be accounted for as a result of pressure, or by supposing that, as the globe cooled, the heavier elements accumulated towards the centre. Both suppositions may be true in part, but less weight is to be placed upon the second, for the following reason: A mixture of the elements in equal proportions, in the free state and as they behave at the earth's surface, would have a specific gravity of about 7.3. In combination, the density would be greater because of condensation, and below the surface it would also be increased by pressure. Hence it seems clear, since the density of the earth is only 5.5, that in the planet as a whole the lighter elements must very considerably exceed in quantity the heavier ones. Twenty-nine of the known elements have densities below 5.5, and forty exceed that figure, iron being the only one of the heavier group which is at all abundant. The greater part of the earth's mass is almost certainly to be found among the twenty-nine lighter elements. The others may be more plentiful at the centre of the globe than on its surface, but few besides iron can be dominant constituents. This evidence seems to be clear, even though it is not proof positive."

Qualitatively. — The metals, in a few cases, exist in the earth in the free — the chemically uncombined — form called *native.* Thus native gold, native silver, and native copper are of common occurrence.

But most of the metals occur in the earth only in a state of combination.

Of binary compounds, oxides and sulphides are most common.

Of ternary compounds, carbonates and silicates are most common.

The ancients were able to recognize only those metals that are ***easily obtained*** in the metallic form. As has been stated, gold, silver, and copper exist in the earth free and uncombined. But certain ores which are ***compounds*** of metals are very easily decomposed so as to yield the metal — ores of lead may be mentioned. Now the ancients knew gold, silver, copper, and a few others, as lead and tin, and even iron.

A few of the metals, as mercury and zinc, were recognized in the middle ages; but most of the metals have been discovered since the opening of the nineteenth century.

By reason of the intense affinities of most of the metals, compounds of these substances were known long before the metals themselves, in a free, elementary condition, were obtained.

Sodium and potassium are examples. A compound of sodium, sodium chloride (common salt) and a mixture of compounds of potassium (potash or purified wood ashes), were known long before even the idea was grasped that special metals existed in them. It is even now a difficult undertaking to withdraw these metals from their compounds.

Again, some metals exist in very minute quantities on this globe, even as compounds; thus irrespective of other conditions, like those above mentioned, it is difficult to obtain them.

Most of the metals were not distinctly recognized until chemistry, as a science, was considerably developed, and until new and peculiar methods for the decomposition or recognition of elementary substances were discovered; indeed, without the new method of investigation called spectrum analysis, or some other equally delicate method of research, many of the metals — and non-metals also — would never have been detected at all.

Preparatory Work Upon Metal-bearing Materials.

A "prospector" or a geologist may discover a natural deposit of material containing a useful metal. A mining engineer may develop the deposit (1) by opening it by appropriate excavations, (2) by bringing the material (in case of *heavy metals* called the ore) to the surface and then delivering it to the metallurgical "mill" in proper condition. A metallurgist or mill superintendent may then subject the raw material to such treatment (generally more or less chemical) as shall result in the extraction of the metal itself.

But the work of each one of these persons may require, in certain cases, a variety of different operations.

First. The excavated material is so sorted, by the process of "ore-dressing," that it is separated into at least two parts: the richer (often called "mineral") and the poorer (often called "rock," and which latter may be treated yet again under the name of "tailings," until that which cannot be employed to advantage is thrown away).

Secondly. The dressed mineral is subjected to processes of "smelting," or "reduction," or "refining," according to the character of the metal sought, and the quality of the metallic product contemplated.

Ore-dressing.

The mechanical methods of ore-dressing depend upon the greater specific gravity of most metal-bearing minerals as compared with quartz and similar comparatively worthless rock material. The ore is crushed; it is then screened so as to divide it into portions of dimensions suitable for the later work. In some cases very fine powder is desired; in other cases fine powder is open to serious objections (it may clog the furnaces, or blow away under the air-blast, or mat down in a roasting furnace).

— In countries where population is dense and labor is cheap, ore is sometimes picked by hand — women and children sorting it. But oftener, large use is made of machines.

— Mechanical apparatus, as "vanners," "jigs," "buddles," and the like, systematically agitate the pulverized ore in a carefully regulated current of water; the water carries off the "tailings" while the machine delivers the valuable "concentrates" into a bin for future use.

Sometimes a current of air is forced at such a rate and through such a series of steel tubes that the lighter portions of rock are carried to the waste heap while the heavier drop into a receiver prepared for them.

It is sometimes profitable to reserve "tailings" for a subsequent metallurgic treatment.

— Magnetic methods are often employed for magnetic iron ores. Edison has worked in New Jersey a magnetic separating system; in this, portions of crushed magnetic iron ore are made to fall through the air on either side of a set of magnets. The magnetic ore is deflected from its natural vertical downward course into a suitable hopper; but the non-magnetic, worthless parts of the powdered rock fall vertically into heaps on either side.*

Extraction of Metals from Ores (Reduction).

The metallurgic methods of extracting metals are classed under dry processes (furnace work), and wet processes (treatment in liquid solutions). In certain cases the dry process is employed up to a certain stage and then the extraction is completed by use of a wet process.

Dry Processes for the Extraction of Metals.

1st. — *By heating an oxide with carbon.* At high temperatures the affinity of carbon for oxygen is such that it may withdraw oxygen from most metallic oxides. Thus, oxide of iron may part with its oxygen when heated in a furnace with carbon; of course the carbon combines with the oxygen.

2d. — *By heating an oxide in a current of hydrogen gas.* The principle in this case is like that of the foregoing. The process is *applicable* to most metallic oxides; but in many cases it is too costly. As an example merely, it may be stated that oxide of copper, heated in a closed tube, in a current of hydrogen gas, loses its oxygen; metallic copper is left.

3d. — *By heating an oxide with metallic sodium or other similar metal.* The principle in this case is the same as in the foregoing

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* *McClure's Magazine*, November, 1897. *The Electrical Engineer*, Oct. 28, 1897.

ones. But the cost of sodium and its like is such that the process is only applicable to compounds of high-priced metals.

4th. — *By heating a sulphide with metallic iron.* Iron has at high temperatures such affinity for sulphur, that it may withdraw the sulphur and liberate the other metal.

5th. — *By more complex chemical operations.* As an example may be cited a reaction of which two compounds of lead are capable at high temperatures: when sulphide of lead and oxide of lead are heated together, the sulphur and the oxygen combine and escape as a gas, sulphur dioxide, SO_2, while the metallic lead is liberated. The operation may be represented by the following equation:

$$\underset{\text{Lead sulphide.}}{PbS} + \underset{\text{Lead oxide.}}{2PbO} = \underset{\text{Metallic lead.}}{3Pb} + \underset{\text{Sulphur dioxide.}}{SO_2}$$

6th. — *By electrolysis of dry mixtures.* In some cases a mixture containing a metallic compound may be fused by addition of heat; then by use of electrodes of iron or of carbon the compound may be decomposed by electricity (electrolysed) with separation of the metal sought. Sometimes the necessary heat is furnished by use of fuel; sometimes by the electric current itself. The production of aluminium by Hall's process is an example of the latter form of this kind of work. (See Aluminium.)

Wet Processes for the Extraction of Metals.

1st. — *By use of a cheap metal.* A solution of copper may be decomposed by scrap iron — metallic copper being liberated.

2d. — *By use of a chemical precipitant.* A solution of gold may be decomposed by ferrous sulphate, $FeSO_4$ (also known as copperas and as green vitriol), metallic gold being liberated.

3d. — *By electrolysis in liquid solutions.* A plate of coarse copper, containing many other substances, may be connected as an anode in a suitable liquid solution, then the electric current may drive all the copper through the solution to a prepared cathode. Thus a plate of pure electrolytic copper may be obtained. Incidentally, and at the same time, the other substances, notably gold and silver, in the original coarse copper, may fall through the solution as a deposit (slime) which may be subsequently refined.

4th. — *By more complex liquid processes.* Examples of these may be found in the Washoe silver process, and the cyanide gold process, and others mentioned later in this book.

Preliminary Roasting of Metallic Ores.

In case of many metallic ores, especially those containing sulphur, a roasting process is conducted with a view of expelling as much as possible of a certain element (for example sulphur) — incidentally the metal may be brought into the form of a much more manageable compound, viz., an oxide or a sulphate, or partly into both.

Roasting is sometimes accomplished in "heaps," or "stalls," the ore being mixed with a moderate supply of fuel. After the fuel has burned, the burning of the sulphur of the ore itself may keep the roasting operation in progress for weeks.

But in many cases finely adjusted furnaces are employed.

Separation of One Metal from Another.

This may be accomplished by heat in the dry way, for example, by *cupellation* of an alloy of lead and silver; or by *acid parting*, for example, by treating certain alloys of gold and silver with an acid, for example, nitric acid or sulphuric acid, which will dissolve the silver and not the gold; or by an electrolytic process where one metal in an alloy (say copper) may be deposited by electricity as a coherent plate, while other metals of the alloy go into solution or settle as muddy solids at the bottom of the tank employed.

Properties of the Metals — Mechanical and Physical Properties.

It is not proposed here to discuss the mechanical and physical properties of metals, such as resistance to mechanical stress, melting points, conducting power for heat, electricity, and the like.

Properties of the Metals — Chemical Properties.

Some of the chemical properties of the metals have been stated already in a general way. It is proposed to discuss these properties here mainly as to the classes of compounds formed.

Chemical Compounds of the Metals with Metals: Alloys.

One interesting property of metals is their tendency to form alloys. Thus, copper and zinc, melted together, form the alloy known as brass. Mercury unites with many other metals to form alloys called amalgams. These alloys themselves possess metallic character so far as their physical properties are concerned.

But it must be distinctly observed that the properties of alloys are not *means* of the properties of the constituent metals: an alloy often has a melting point below that of any of its constituent metals.

Thus tin (melting point, 451° F.), bismuth (melting point, 515° F.), cadmium (melting point, 608° F.), and lead (melting point, 619° F.), may be made into an alloy, the so-called fusible alloy, whose melting point is 160° F. — a temperature below the boiling point of water.

Chemical Compounds of the Metals with the Non-Metals: Salts.

Metals combine with non-metals under a variety of conditions, by a variety of methods — and form a variety of products. Only the products will be discussed here. These products are very numerous, and they may be grouped in many different classes. They are often looked upon as substitution compounds — products arising from some other compound by the substitution of a metal for some element or radicle existing in the initial compound. The commonest form of such substitution is that in which a metal displaces hydrogen.

Binary compounds with non-metallic monads. — Compounds of metals with hydrogen are known; but they are not common. While the non-metallic elements incline strongly to combine with hydrogen, the distinctly metallic elements show but slight tendency of this kind.

Compounds of metals with fluorine, chlorine, bromine, and iodine, respectively, are very common. They are viewed as formed by the proper substitution of a metallic element for the hydrogen of hydrofluoric acid, HF, of hydrochloric acid, HCl, or of hydrobromic acid, HBr, or of hydiodic acid, HI, respectively. Examples are:

Calcium fluoride,	CaF_2
Sodium chloride,	$NaCl$
Potassium bromide,	KBr
Lead iodide,	PbI_2

Compounds of this type are called in general, salts, and more definitely, haloid salts.

Binary compounds with non-metallic dyads.— Probably every metal may be caused to unite with oxygen ; though some metals do so with far greater readiness than others.

— In most cases a given metal may form more than one oxide. Generally the oxides of metals are basic anhydrides ; that is, they combine with water to form bases (called also hydrates and hydroxides). On the other hand the non-metals form oxides which are acid anhydrides ; that is, they may combine with water to form acids.

Thus, the metal sodium, Na, may form sodium oxide, Na_2O ; this may combine with water : $Na_2O + H_2O = 2NaOH$. Now the substance designated by the formula, NaOH, belongs to the general class of bases (its particular names are sodium hydrate, or sodium hydroxide, or caustic soda).

On the other hand the non-metal sulphur, S, may form sulphur trioxide, SO_3 ; this may combine with water : $SO_3 + H_2O = H_2SO_4$. Now the substance designated by the formula, H_2SO_4, belongs to the general class of acids (its particular names are hydrogen sulphate, or sulphuric acid, or oil of vitriol).

— Several of the metals form oxides called peroxides which are not basic anhydrides, for they do not unite with water to form bases. Thus, the metal manganese, Mn, may form an oxide called manganese peroxide (also manganese dioxide), MnO_2. This is not a basic anhydride.

— Several of the metals may form highly oxidized oxides, which are acid anhydrides, for they may unite with water to form acids. Thus the metal manganese, Mn, may form an oxide, called manganic anhydride, MnO_3 ; this may unite with water thus :

$$MnO_3 \quad + \quad H_2O \quad = \quad H_2MnO_4$$

Now the substance designated by the formula H_2MnO_4 belongs to the general class of acids (its particular name is manganic acid).

Most of the metals combine with selenium and tellurium. The known compounds of these elements are not as numerous as those with oxygen, but so far as known they are of the same types — they correspond closely with the oxygen compounds already referred to. Thus sulphur forms sulphides which act either as sulphur bases, or as persulphides, or as acid-forming sulphides. Selenium and tellurium act in similar fashion.

Binary compounds with non-metallic triads. — Compounds of metals with boron forming borides, with nitrogen forming nitrides, with phosphorus forming phosphides, with arsenic forming arsenides, with antimony forming antimonides, are known. Some of them are of special interest; but such compounds are not largely used.

Binary compounds with non-metallic tetrads. — Many of the metals are capable of combining with carbon to produce binary compounds called carbides. Such carbides are best formed by heating the metal with carbon in an electric furnace. The existence of metallic carbides at positions far below the surface of the earth is believed; but most metallic carbides known are artificial. Cast-iron and steel are carbides; so is spiegeleisen.

Many of the metals are capable of combining with silicon to produce silicides.

Double compounds of the foregoing classes. — A great many metals may produce binary compounds with more than one metal, or with more than one non-metal, at once. In some cases such double compounds are of considerable interest to chemists. The following examples may serve at this point:

Potassio-platinic chloride,	K_2PtCl_6
Potassium silico-fluoride,	K_2SiF_6

Salts. — Reference has been made, thus far, to *haloid salts*. The metals are also capable of forming *ternary salts*. A ternary salt may be looked upon as produced by the substitution of a metal for the hydrogen of an acid. Thus, when zinc is added to sulphuric acid the zinc takes the place of the hydrogen in the acid. The change may be expressed as follows:

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

But zinc sulphate may be *looked upon* as produced by the union of the basic anhydride, zinc oxide, ZnO, with the acid anhydride, sulphur trioxide, SO_3:

$$ZnO + SO_3 = ZnSO_4$$

Normal salts, acid salts, basic salts, and double salts. — When a metal *fully replaces the hydrogen of an acid*, the product is called a normal salt. Thus in the salt, potassium sulphate, K_2SO_4, the metal potassium, K, is viewed as having replaced all of the hydrogen of the acid, sulphuric acid, H_2SO_4. The salt, potassium sulphate, K_2SO_4, is called a normal salt.

When a metal *partially replaces the hydrogen of an acid*, the product is called an acid salt. Thus in the salt, hydro-potassium sulphate, $HKSO_4$, the metal potassium, K, is viewed as having replaced only a part of the hydrogen of the acid, sulphuric acid, H_2SO_4. The salt, hydro-potassium sulphate, $HKSO_4$, is called an acid salt. Acid salts are partly acid, and partly salt.

When an acid radicle *partially replaces the hydrogen of a base* the product is called a basic salt. Thus in the salt, lead nitrohydrate, Pb, OH, ONO_2, the acid radicle NO_2 of nitric acid is viewed as having replaced only a part of the hydrogen of the base lead hydroxide, $Pb(OH)_2$. The salt mentioned is called a basic salt. Basic salts are partly base, and partly salts.

The following table will assist in displaying the relationships of acids, bases, acid salts, basic salts, and normal salts to one another :

Acid,	$\begin{matrix}H—O—\\H—O—\end{matrix}SO_2$	Base,	$Pb\begin{matrix}—O—H\\—O—H\end{matrix}$
Acid salt,	$\begin{matrix}H—O—\\K—O—\end{matrix}SO_2$	Basic salt,	$Pb\begin{matrix}—O—H\\—O—NO_2\end{matrix}$
Normal salt,	$\begin{matrix}K—O—\\K—O—\end{matrix}SO_2$	Normal salt,	$Pb\begin{matrix}—O\ NO_2\\—O—NO_2\end{matrix}$

Double Salts. — In some cases a salt containing a given metal may be made to unite with a salt containing another metal, and so produce a much more complicated salt — which, however, is a proper unit of itself. One of the best examples of double salts is found in alum.

Ordinary alum is called potassium aluminium sulphate. It has the formula, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. This substance is viewed as a chemical compound of the normal salt, potassium sulphate, K_2SO_4, and the normal salt, aluminium sulphate, $Al_2(SO_4)_3$, (plus twenty-four molecules of water of crystallization). The salt mentioned, long known as alum, is one of an extended series of salts of similar type, all of which are called alums. They have certain properties in common. But different alums have different constituents within certain limits; they may possess different special properties also — such as different colors.

Water of crystallization. — In a multitude of cases, when the solution of a salt in some liquid is evaporated, or, it may be, is merely cooled, portions of the salt gradually separate and fall out of the liquid in the solid form. When the operation proceeds favorably, the solid salt appears as crystals. As it separates from a water solution, the salt often contains water, combined as a part of the solid, in a form called water of crystallization.

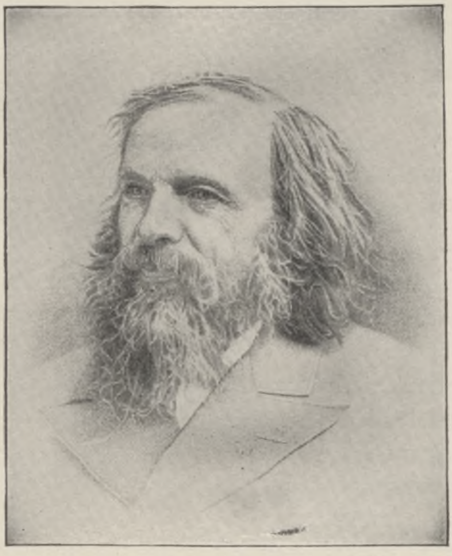
Under definite conditions the amount of water of crystallization is definite; it is generally less when crystallization proceeds at higher temperatures: thus the normal metallic salt, sodium sulphate, Na_2SO_4, may at varying temperatures crystallize with amounts of water of crystallization varying from none to ten molecules, and so form at least three different solid crystalline salts:

Anhydrous sodium sulphate,	Na_2SO_4
Heptahydrated sodium sulphate,	$Na_2SO_4 \cdot 7H_2O$
Dekahydrated sodium sulphate,	$Na_2SO_4 \cdot 10H_2O$

More complex compounds. — Metals may enter into *organic* compounds as constituents. Thus many very complex types of molecules may be formed.

Order of Discussion of the Metals.

In this book, the metals are discussed in eight periodic groups. The classification is based upon the chemical properties of the elements, and especially upon Mendeléeff's periodic table.



Dmitri Mendeléeff (Distinguished Russian Chemist).

MENDELÉEFF'S PERIODIC TABLE OF ELEMENTS.

(Using Approximate Numbers.)

GROUPS.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
R_2O	R_2O_2 or RO	R_2O_3	RH_4 R_2O_4 or RO_2	RH_3 R_2O_5	RH_2 R_2O_6 or RO_3	RH R_2O_7	R_2H etc. R_2O_3 or RO_4 etc.
1 H Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
23 Na K 39	24 Mg Ca 40	27 Al Sc 44	28 Si Ti 48	31 P V 51	32 S Cr 52	35 + Cl Mn 55	Fe 56 Ni 59 Co 59
63 Cu Rb 85	65 Zn Sr 87	69 + Ga Y 89	72 Ge Zr 90	75 As Cb 93	79 Se Mo 96	80 Br	Ru 101 Rh 103 Pd 106
108 Ag Cs 133	112 Cd Ba 137	114 In La 138	119 Sn Ce 140	120 Sb Nd 141 Pr 144	127 Te	127 I Sm 150	
		Yb 173		166 E Ta 183	W 185		Os 190 Ir 193 Pt 195
197 Au	200 Hg	204 Tl	207 Pb Th 233	208 Bi	U 240		

The best known members of the several groups are mentioned in a list below; but the more or less rare metals of the several groups (not mentioned here) are discussed hereafter in their proper places:

First group,	lithium, sodium, potassium ; copper, silver and gold.
Second "	calcium, strontium, barium ; magnesium, zinc, mercury.
Third "	the rare yttrium metals ; aluminium.
Fourth "	tin, lead.
Fifth "	bismuth.
Sixth "	chromium.
Seventh "	manganese.
Eighth "	iron, nickel, cobalt ; also platinum and its allied metals.

Sir William Crookes suggests a valuable and instructive method of arranging the elementary substances in an orderly sequence. The arrangement is somewhat different from that of Mendeléeff, but it embodies many of the same important features. Crookes' method requires a model of three dimensions for its full presentation, but the table given below affords some notion of it :

SIR WILLIAM CROOKES' PERIODIC (LEMNISCATE) TABLE, WITH APPROXIMATE ATOMIC WEIGHTS.

(*Chemical News*, 78 : 25.)

H 1	He 4	Li 7	Gl 9	B 11	C 12	N 14	O 16	F 19	Na 23	Mg 24	Al 27	Si 28	P 31	S 32
Cl 35+	Ar 39+	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn, Fe, Ni, Co 55, 56, 59, 59	Cu 63	Zn 65	Ga 69+	Ge 72	As 75	Se 79
Br 80	Kr 80	Rb 85	Sr 87	Yt 89	Zr 90	Nb 93	Mo 96	Rh, Ru, Pd 103, 101, 106	Ag 108	Cd 112	In 114	Sn 119	Sb 120	Te 127
I 127		Cs 133	Ba 137	La 138	Ce 140	( )	( )	( )	( )	( )	( )	( )	( )	( )
( )		( )	( )	( )	( )	Ta 183	W 185	Ir, Pt, Os, 193, 195, 190	Au 197	Hg 200	Tl 204	Pb 207	Bi 208	
					Th 233		U 240							

The parentheses suggest places, as yet not definitely assignable, for known elements of the neodymium and erbium groups.

List of Typical Compounds Formed by a few of the Metals.

FIRST PERIODIC GROUP.

Lithium chloride	$LiCl$
Sodium oxide	Na_2O
“ hydroxide	$NaOH$
“ dioxide	Na_2O_2
“ carbonate	Na_2CO_3
Hydro-sodium carbonate	$HNaCO_3$
Sodium nitrite	$NaNO_2$
Sodium tetra-borate	$Na_2B_4O_7$
Potassium iodide	KI
“ chlorate	$KClO_3$
“ perchlorate	$KClO_4$
Hydro-potassium sulphate	$HKSO_4$
Ammonium chloride	$(NH_4)Cl$
“ hydroxide	$(NH_4)OH$
Cupric oxide	CuO
Cuprous “	Cu_2O
Silver bromide	$AgBr$
“ nitrate	$AgNO_3$
Auric chloride	$AuCl_3$

SECOND PERIODIC GROUP.

Calcium fluoride	CaF_2
“ sulphite	$CaSO_3$
“ silicate (wollastonite)	$CaSiO_3$
Calcium hypochlorite	$Ca(ClO)_2$
“ chlorite	$Ca(ClO_2)_2$
“ phosphate	$Ca_3(PO_4)_2$
Hydro-calcium phosphate	$H_4Ca(PO_4)_2$
Strontium chloride	$SrCl_2$
Strontium nitrate	$Sr(NO_3)_2$
Barium chloride	$BaCl_2$
“ sulphate	$BaSO_4$
Magnesium chloride	$MgCl_2$
“ carbonate	$MgCO_3$
Zinc chloride	$ZnCl_2$
“ carbonate	$ZnCO_3$
Mercuric chloride (corrosive sublimate).	$HgCl_2$
Mercurous chloride (calomel).	Hg_2Cl_2

THIRD PERIODIC GROUP.

Aluminium oxide	Al_2O_3
“ sulphate	$Al_2(SO_4)_3$
Potash alum	$K_2SO_4.\ Al_2(SO_4)_3.\ 24H_2O$

FOURTH PERIODIC GROUP.

Stannous chloride	$SnCl_2$
Stannic “	$SnCl_4$
Sodium stannate	Na_2SnO_3
Lead chloride	$PbCl_2$
“ iodide	PbI_2
“ oxide	PbO
“ di-oxide	PbO_2
“ nitrate	$Pb(NO_3)_2$
“ sulphate	$PbSO_4$

FIFTH PERIODIC GROUP.

Bismuth chloride	$BiCl_3$
Bismuthyl “	$(BiO)Cl$
“ nitrate	$(BiO)NO_3$

SIXTH PERIODIC GROUP.

Chromic chloride	Cr_2Cl_6
Cromium trioxide	CrO_3
Potassium chromate	K_2CrO_4
“ di-chromate	$K_2Cr_2O_7$

SEVENTH PERIODIC GROUP.

Manganous chloride	$MnCl_2$
“ oxide	MnO
Manganese di-oxide	MnO_2
Manganic oxide	Mn_2O_3
Manganese trioxide	MnO_3
Potassium manganate	K_2MnO_4
“ permanganate	$K_2Mn_2O_8$

EIGHTH PERIODIC GROUP.

Ferrous chloride	$FeCl_2$
“ oxide	FeO
“ sulphate	$FeSO_4$
Ferric chloride	Fe_2Cl_6
“ oxide	Fe_2O_3
“ sulphate	$Fe_2(SO_4)_3$
Platinum di-chloride	$PtCl_2$
“ tetra-chloride	$PtCl_4$
Ammonio-platinic chloride	$(NH_4)_2PtCl_6$

Appendix to Introduction.—New or Doubtful Elements.

LIST OF ELEMENTARY SUBSTANCES, ANNOUNCED SINCE 1877.

Extended from the list prepared by Dr. H. Carrington Bolton.

DATE.	NAME.	SOURCE.	DISCOVERER.	REFERENCES.
1877	Neptunium	Columbite	Hermann	Chem. News, 35 : 197.
"	Lavoesium	Pyrite	Prat.	
"	Mosandrum	Samarskite	J. Lawrence Smith	Chem. News, 38 : 61, 231, 287.
"				Chem. News, 36 : 4, 114, 155, 164; 37 : 65.
"	Davyum	Platinum ores	Sergius Kern	
1878	New earths	Unnamed mineral	Gerland	
"	"X"	Gadolinite	Soret	
"	Philippium	Samarskite	Delafontaine	Chem. News, 38 : 202.
"	Decipium	Samarskite	Delafontaine	Chem. News, 38 : 123, 44 : 67.
"	Ytterbium	Gadolinite	Marignac	Chem. News, 42 : 61, 184.
1879	Scandium	Gadolinite	Nilson	Chem. News, 40 : 76, 159.
"	Norwegium	Gersdorffite	Dahll	Chem. News, 40 : 25, 41 : 116.
"	Uralium	Platinum	Guyard	Chem. News, 40 : 57.
"	Samarium	Samarskite	DeBoisbaudran	Chem. News, 48 : 39, 74.
"	Barcenium			Wagner, J., 1879 : 8.
"	Thulium	Gadolinite	Cleve	Chem. News, 42 : 185.
"	Holmium	Gadolinite	Cleve	Chem. News, 40 : 224; 40 : 125, 147.
"	Columbium	Samarskite	J. Lawrence Smith	Nature, 21 : 146.
"	Rogerium	Samarskite	J. Lawrence Smith	
"	Vesbium	Lava	Scacchi	Chem. News, 41 . 116.
1880	Comesium		Kaemmerer	
"	Y alpha and Y beta	Gadolinite	Marignac	
1881	Actinium	Zinc ores	Phipson	Chem. News, 44 : 138, 191.
1882	Didymium beta	Gadolinite	Cleve	Chem. News. 47 : 203; 52 : 227, 255, 264, 271, 278, 291.
1883	Nameless	Platinum ores	Th. Wilm	
1884	Idunium	Vanadinite	Websky	
1885	Praseodymium	Didymium	A. v. Welsbach	Chem. News, 52 : 49.
"	Neodymium	Didymium	A. v. Welsbach	
"	Z alpha	Didymium	DeBoisbaudran	Chem. News, 53 : 217.
"	Z beta	Didymium	DeBoisbaudran	
"	Germanium	Argyrodite	C. Winkler	Chem. News, 54 : 135.
1886	Z gamma	Terbia	DeBoisbaudran	
"	Dysprosium		DeBoisbaudran	Comptes R., 102 : 1003.
"	Gadolinium		Marignac	Comptes, R.
"	Eleven provisional names	Gadolinite and Samarskite	Crookes	Chem. News, 54 : 15.
"	Polymnestum	Various Scotch rocks	A. Pringle	Chem. News, 54 : 167.
"	Erebodium			
"	Gadenium			
"	Hesperisium			
"	Two not named			
1889	Russium		Chrustschoff	Science, 14 : 131.
"	Austrium	Tellurium	Brauner	Chem. News, 59 : 295.
"	Gnomium	Cobalt, nickel	Krüss & Schmidt	Nature, 40 : 67.
"	"X"	Tellurium, antimony and copper	A. Grünwald	Chem. News, 61 : 39.
1892	Masrium	Egyptian mineral	H. D. Richmond and H. Off	Chem. News, 63 : 246.

APPENDIX TO INTRODUCTION — *Continued.*

DATE.	NAME.	SOURCE.	DISCOVERER.	REFERENCES.
1894	Argon	Atmospheric air	Lord Rayleigh and W. Ramsay	Jour. Am. Ch. Soc., 19 : 124.
"	Helium			
1896	Lucium	Monazite sand	P. Barière	Chem. News, 74; 159, denied by W. Crookes. Chem. News, 74 : 259.
1897	Bythium	Sulphur	Th. Gross	Chemiker Zeitung xxi-35, May 1, 1897.
1898	Krypton	Atmospheric air	W. Ramsey and M. W. Travers.	Chem. News, 77 : 270, 287; 78 : 1, 154. Sci. Am., 79 : 114,
"	Metargon			
"	Neon			
"	Xenon			
"	Coronium	Volcanic gases	Nasini, Anderlini, and Salvadori	Chem. News, 78 : 43.
"	Etherion	Atmospheric air	C. F. Brush	Sci. Am., 79 : 147.
"	Polonium	Pitch blende	M. & Mme. Curie	Chem. News, 78 : 133.
"	Monium	Yttrium earths	Wm. Crookes	Chem. News, 78 : 134.
"	Radium	Pitchblende	P. Curie, and others	Chem. News, 79 : 1.
1899	Victorium (New name for Monium.)	Yttrium earths	Wm. Crookes	Chem. News, 79 : 212; 80 : 49.

BOOK I. — FIRST PERIODIC GROUP.

1st Section. — LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, CAESIUM, (AMMONIUM).

2d Section. — COPPER, SILVER, GOLD.

General Comments on the Group.

The elementary substances of this group are classed together because they possess certain fundamental resemblances — both physical and chemical. These may be shown, to some extent, by a consideration of the true metals of the first section (excluding for the moment the compound *hypothetical* metal ammonium).

Physically several of the metals show marked and progressive similarities: They are softer than lead, and they are of very low specific gravity, three of them being lighter than water, and one of these, lithium, being the lightest *solid* known.

Density of metallic lithium = .58 (water being 1)
sodium = .98
potassium = .86
rubidium = 1.52
caesium = 1.88

Their atomic weights show certain striking relationships; that of sodium being almost exactly intermediate between those of lithium and potassium; and that of rubidium being almost exactly intermediate between those of potassium and caesium:

Atomic weight of lithium = 7.03 (Oxygen = 16)
sodium = 23.05
potassium = 39 11
rubidium = 85.43
caesium = 132.89

Chemically, the five elements mentioned show striking similarities: they manifest extreme activity; they form compounds of similar types; their compounds have similar properties.

The metals rapidly oxidize in air of ordinary temperature, while at slightly elevated temperatures they burn with flame; as a result of such oxidation they form oxides of corresponding types:

Lithium oxide, Li_2O; sodium oxide, Na_2O; potassium oxide, K_2O; (but rubidium oxide, Rb_2O, and caesium oxide, Cs_2O, have not yet been isolated).

— Again, the oxides easily dissolve in water, producing hydroxides of similar molecular type and of similar chemical properties:

Lithium hydroxide, LiOH; sodium hydroxide, NaOH; potassium hydroxide, KOH; rubidium hydroxide, RbOH; caesium hydroxide, CsOH.

— The hydroxides are also readily produced when the respective metals are thrown upon water at ordinary temperature; they are all *alkalies:* they have an acrid, burning taste, and they turn litmus from the red to the blue color.

— When compounds of these metals are heated they easily yield light of a characteristic color: lithium salts emit crimson light, sodium salts emit orange light, potassium salts emit a pinkish violet light.

— Many other physical and chemical relationships of the elements themselves or of their corresponding chemical compounds might be cited.

LITHIUM, Li; 7,03.

Distribution — Preparation — Properties — Compounds.

Data for Reference.

Density of solid lithium, .5891—.5983 (water being the standard = 1).

Fusing point of solid lithium, 180° C.

Boiling point of liquid lithium, (the metal takes fire at temperature but slightly above its fusing point).

Lithium was discovered by Aug. Arfvedson in 1817.

The word lithium is derived from a Greek word, λίθος (*lithos*), a stone.

Distribution of Lithium.

Lithium is never found free and uncombined. Lithium compounds are comparatively rare in the earth, but they are very widely diffused.

When the salts of lithium were first discovered, it was not supposed that the metal was widely distributed. Spectrum analysis, however, has been able to prove that it exists in a great many substances where it was not at first suspected. For instance, it has been found in small quantities in milk, in tobacco, in human blood.

The principal minerals containing lithium are lithium mica, called *lepidolite*, and an aluminium lithium silicate, called *petalite*:

		Lepidolite.	Petalite.
Silicon dioxide,	SiO_2	40 — 54 per cent.	77 — 79 per cent.
Aluminium oxide,	Al_2O_3	20 — 38 "	15 — 18 "
Lithium oxide,	Li_2O	1 — 5 "	2 — 6 "

— But lepidolite may also contain compounds of iron, manganese, magnesium, sodium, and potassium.

Salts of lithium are also found in certain mineral waters. In Cornwal , England, is a mineral spring whose waters contain considerable quantities of lithium. In the United States, also, mineral waters containing varying quantities of lithium are tolerably widely diffused. Such waters are much sought after, since the lithium salts contained in them are supposed to have certain distinct medicinal qualities.

While very few mineral springs possess *considerable quantities* of lithium salts, a great many mineral waters contain it in minute quantities — but such as are easily detected by the spectroscope.

Preparation of Lithium.

Metallic lithium may be prepared by electrolysis. The electric current acting on the fused lithium chloride, $LiCl$, decomposes the salt and yields the metal.

Properties of Lithium — Physical Properties.

Metallic lithium is a soft but tough metal with a silver-white color. It is harder than potassium and sodium ; it is softer than lead. Its specific gravity is very low, .59 (but little more than half as heavy as water) ; in fact, it is the lightest *solid* substance known.

Properties of Lithium — Chemical Properties.

The metal lithium has great chemical activity. At ordinary temperatures it acts on water decomposing the latter as sodium and potassium do, only less violently.

One of the interesting properties of lithium and its compounds is their power of producing a rich crimson light when they are highly heated. Such light, when examined by the spectroscope, is seen to produce a spectrum having a single prominent red line.

Compounds Containing Lithium.

As already stated, lithium salts resemble potassium and sodium salts in some respects. Two of the compounds of lithium, however, differ distinctly from those of potassium and sodium. The carbonate of lithium, Li_2CO_3, and the phosphate of lithium, Li_3PO_4, are not readily soluble in water; but the corresponding carbonates and phosphates of potassium and sodium are readily soluble in water.

A Few Compounds of Lithium (with elements already discussed).

With fluorine;	Lithium fluoride,	LiF		
With chlorine;	" chloride,	LiCl		
With bromine;	" bromide,	LiBr		
With iodine;	" iodide,	LiI		
With oxygen;	Lithium oxide,	Li_2O; LiO_2?	Lithium hydroxide,	LiOH
With sulphur;	Lithium sulphide,	Li_2S;	Lithium sulphate,	Li_2SO_4
			——— hydrogen sulphate,	$LiHSO_4$
			——— potassium sulphate,	$LiKSO_4$
With boron;	Lithium borofluoride,	$LiBF_4$	Lithium borate,	$Li_2B_4O_7$
With nitrogen;			Lithium nitrate,	$LiNO_3$
With phosphorus;			Lithium phosphate,	Li_3PO_4
			——— di-hydrogen phosphate,	LiH_2PO_4
With antimony;			Lithium antimonate,	$LiSbO_3$
With carbon;			Lithium carbonate,	Li_2CO_3
			——— hydrogen carbonate,	$LiHCO_3$
With silicon;	Lithium silicofluoride,	Li_2SiF_6;	Lithium silicate,	Li_4SiO_4

SODIUM, Na; 23,05.

Introduction — Distribution, preparation, and properties of sodium — Compounds of sodium, especially the chloride, oxide, sulphate, borate, carbonate, phosphate, silicate.

First appendix — The alkali trade.
Second appendix — Glass.

Data for Reference.

Density of solid sodium, .9735 (water being the standard = 1).
Fusing point of solid sodium, 95.6° C.
Boiling point of liquid sodium, 861° — 954°.
Sodium was discovered by Sir Humphry Davy in 1807.
The word sodium is a manufactured word of Latin form derived from the word soda.

Introduction.

Certain compounds of sodium, of which common salt is the best example, have been known from ancient times. But for a very long time it was not known that these substances contain a special metal — indeed, the very idea of a chemical compound was not clearly defined until toward the close of the XVIIIth century.

The discovery of oxygen in 1774 was followed by a period of ardent study of chemistry. About this time the thought was advanced that certain substances, previously undecomposed, are composite, and that they contain metallic constituents. This idea was verified by the work of Sir Humphry Davy. In 1807 he discovered several new metals, among them sodium. He discovered this meta by electrolysis of certain of its compounds.

Distribution of Sodium.

Free, *uncombined sodium* is not known to occur naturally on this planet.

But *sodium compounds* are found very widely distributed.

Common salt, sodium chloride, NaCl, is the most familiar and common natural compound of sodium; from it most of man's different sodium compounds (and the largest *amounts* of sodium compounds) are manufactured.

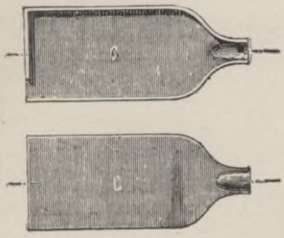


Fig. 3.

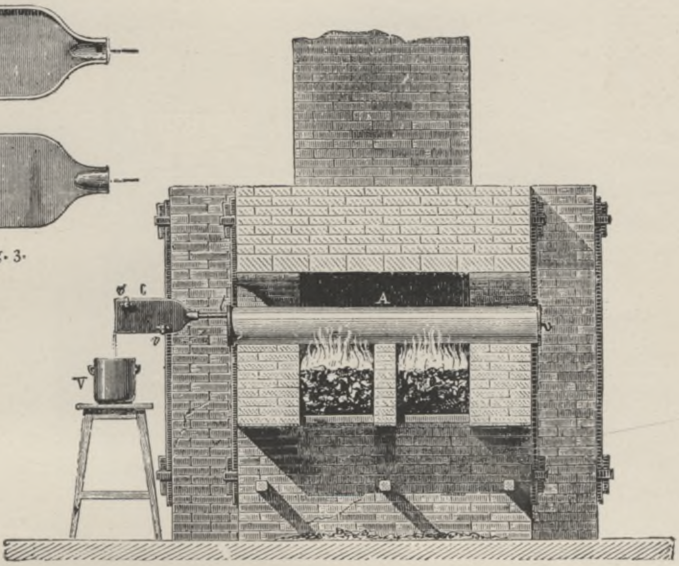


Fig. 2. Furnace for production of metallic sodium. A mixture of sodium carbonate and carbon is heated in the cylindrical retort. Metallic sodium distils as vapor. It is collected in the solid form in the receiver C.

Fig. 3 (above). Details ot receiver for collecting sodium (see Fig. 2). It is made of two plates ot metal clamped together. Its flat form favors cooling of the sodium vapors.

— Common salt is the chief mineral constituent in sea water. Smaller quantities of salt exist in waters ordinarily called fresh — river water, for example. It exists in many parts of the earth in solid deposits called rock salt. The brine of many mineral springs also contains it.

— Many solid mineral compounds contain sodium in combination with other elements.

— Most growing plants contain sodium compounds. Somewhat as potassium compounds are the characteristic compounds of the ashes of land plants, sodium compounds are the characteristic constituents of the ashes of marine plants.

— Sodium compounds are found in small quantities in many living animals.

Preparation of Sodium.

1 — Metallic sodium has been prepared by a process similar to that employed in the preparation of other metals. The general principle involved is this : Some oxidized compound of the metal is heated in contact with carbon. At high temperatures the carbon withdraws the oxygen and liberates the metal.

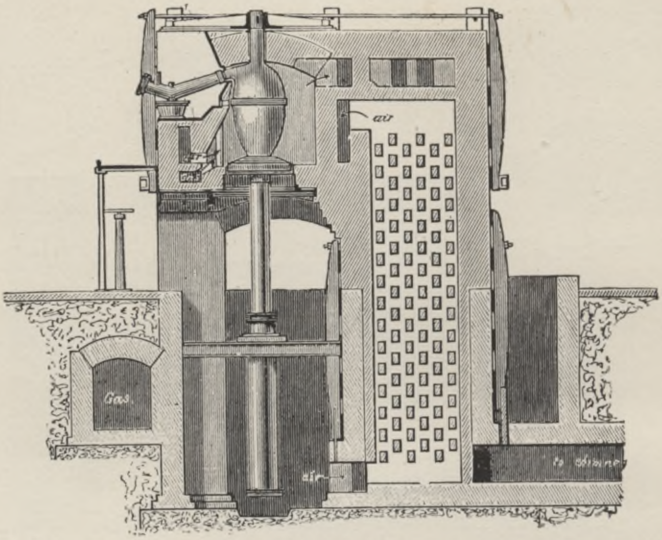


Fig. 4. Section of Castner sodium furnace. It is heated by gas which passes through the checker-work. The top of the retort is fixed — the bottom may be lowered, the plunger support sinking in the hydraulic pump shaft below it. This pump is operated by the valve-wheel at the left. The retort is charged with sodium hydroxide and carbide of iron.

2 — Castner improved this process ; in his first improvement sodium hydroxide (caustic soda), NaOH, and carbide of iron are heated together in a peculiar, crucible-shaped retort. Sodium is produced and it passes in vapor into the neck of the retort, where it condenses and is afterwards collected :

$$6NaOH + FeC_2 = 2Na_2CO_3 + 3H_2 + 2Na + Fe$$

3 — Castner now makes sodium by electrolyzing fused sodium hydroxide (caustic soda), NaOH.

Properties of Sodium — Physical Properties.

Sodium is a silvery white metal resembling potassium. It is lighter than water. It is soft and easily cut with a penknife. It melts and volatilizes readily.

Sodium is often protected from oxygen in bottles containing petroleum oil. In well-closed vessels, however, considerable portions of sodium may be kept without any oil. The small amount of oxygen in the air-space is quickly absorbed by the sodium, forming a white coat of oxide on the surface of the metal. Oxidation then practically ceases.

Properties of Sodium — Chemical Properties.

— Sodium has very strong electro-positive qualities.

— Upon exposure to the air it readily oxidizes, as does potassium. Sodium then forms sodium oxide, Na_2O. When gently heated in the air it takes fire, burning with a striking orange flame, and giving off a white smoke, consisting mainly of sodium oxide, Na_2O. When heated in a suitable vessel and then subjected to a current of warm air, properly adjusted, it forms sodium dioxide (sodium peroxide), Na_2O_2.

— The affinities of sodium for oxygen and other electro-negative substances are so strong that it easily draws the oxygen or other electro-negative substances from the metals with which they are combined. Such metals are then brought to the metallic condition. Thus sodium is largely used for the production of certain other metals, as magnesium, for example. Again, Castner's process of preparing sodium was devised as a subordinate step to the production of aluminium. (But the invention of the cheaper electrolytic process of producing aluminium has led to the suspension of the use of sodium for this particular undertaking.)

Potassium is capable of liberating many metals in a manner similar to that just stated; but since potassium is more costly than sodium, the latter is employed when practicable.

Fig. 5. Exterior view of Castner sodium furnaces.

Compounds Containing Sodium.

Many compounds containing sodium are known to chemists ; a large number of them are of great practical importance. A few of the more noteworthy compounds are mentioned in the following list :

A Few Compounds of Sodium (with elements already discussed).

With hydrogen ;	Sodium hydride,	Na_4H_2		
With fluorine ;	Sodium fluoride,	NaF ;	Sodium hydrogen fluoride,	$NaHF_2$
With chlorine ;	Sodium chloride,	NaCl ;	Sodium aurochlorate,	$NaAuCl_4$
With bromine ;	Sodium bromide,	NaBr	——— aurobromate,	$NaAuBr_4$
With iodine ;	Sodium iodide,	NaI		
With oxygen ;	Sodium monoxide,	Na_2O ;	Sodium hydroxide,	NaOH
	——— peroxide,	Na_2O_2 ;	Sodium hypochlorite,	NaOCl
			——— chlorate	$NaClO_3$
With sulphur ;	Sodium sulphide,	Na_2S ;	Sodium hydrosulphide,	NaSH
		Na_2S_2		
		Na_2S_3 ;	Sodium sulphite (normal),	Na_2SO_3
		Na_2S_4 ;	——— hydrogen sulphite (acid),	$NaHSO_3$
			——— hyposulphite ?	$NaHSO_2$
			——— disulphite,	$Na_2S_2O_5$
			Sodium sulphate (normal),	Na_2SO_4
			——— hydrogen sulphate (acid),	$HNaSO_4$
			——— disulphate,	$Na_2S_2O_7$
With selenium ;	Sodium selenide,	Na_2Se ;	——— thiosulphate,	Na_2SO_3S
		Na_2Se_2		
With boron ;			Sodium othroborate,	Na_3BO_3
			——— pyroborate,	$Na_2B_4O_7$
			Octahedral borax,	$Na_2B_4O_7 \cdot 5H_2O$
			Prismatic ———	$Na_2B_4O_7 \cdot 10H_2O$
			Sodium metaborate,	$NaBO_2$
With nitrogen ;	Sodamide,	NH_2Na ;	Sodium nitrite,	$NaNO_2$
			——— nitrate,	$NaNO_3$
With phosphorus ;			Sodium hypophosphite,	NaH_2PO_2
			——— orthophosphate,	Na_3PO_4
			——— dihydrogen orthophosphate,	H_2NaPO_4
			Disodium hydrogen orthophosphate,	HNa_2PO_4

With phosphorus — Continued. Sodium mono metaphosphate, Na_2PO_3
—— di —— $Na_2P_2O_6$
—— tri —— $Na_3P_3O_9$
—— tetra —— $Na_4O_4P_4O_8$
—— hexa —— $(Na_6O_6P_6O_{12})$
Sodium pyrophosphate (normal), $Na_4P_2O_7$
—— dihydrogen, $Na_2H_2P_2O_7$

With arsenic; (The compounds closely correspond to those with phosphorus.)

With carbon; Sodium carbonate (normal), Na_2CO_3
—— hydrogen carbonate (acid), $HNaCO_3$

With silicon; Sodium silico-fluoride, Na_2SiF_6
Sodium tetrasilicate, $Na_2Si_4O_9$

Sodium Chloride, NaCl.

Distribution. — This substance occurs as a solid in many parts of the world, notably in Cheshire in England, at Wielizca in Galicia, at Stassfurt in Germany also in the states of Michigan, New York, Virginia, Kansas, Nevada, and Louisiana, and elsewhere.

The material of these deposits is in some cases so nearly pure that it may be pulverized and immediately used (this is true of the Louisiana deposit). Oftener the material contains impurities which must be removed by special processes.

— Common salt exists (in common with many other compounds) in the brine of the ocean. The oceans (and the seas which lack outlets) are great evaporating basins. River waters, charged with varying amounts of impurities, flow into the oceans — but the water constantly escapes by evaporation, leaving the impurities behind.

While the total amounts of solids held in ocean waters appear to be different in different latitudes and longitudes, the constituents appear to be constant in their proportions (except when *depth* is considered).

Thus the colder oceans have less mineral matter; the warmer oceans have more. The Mediterranean is subject to relatively slight circulation and large evaporation; it is relatively rich in salts.

It appears probable, however, that ocean waters from great depths have relatively more calcium compounds than those taken nearer the surface.

Following is a general statement on this point:

	Total Mineral Matter.	
Baltic Sea	1.771	per cent.
Black Sea	1.760	"
Atlantic Ocean, Cape Horn	3.480	"
" " near the Equator	3.570	"
" " 40° 18′ N — 36° 28′ W	3.840	"
Mediterranean Sea	3.770	"
" " (another place)	4.070	"
Dead Sea	27.813	"

While it is difficult to reach exact data, the following may be presented tentatively as the average composition of the water of the larger oceans :

Water	96.470	per cent.
Sodium chloride	2.745	"
Other substances	.785	"
	100.000	"

Again the average composition of the salts may be stated as follows :*

Sodium chloride	77.758	per cent.
Magnesium chloride	10.878	"
Magnesium sulphate	4.737	"
Calcium sulphate	3.600	"
Potassium sulphate	2.465	"
Magnesium bromide	.217	"
Calcium carbonate	.345	"
	100.000	"

It is not easy to account for the large amount of *salt in sea water*. Some chemists have suggested that the water of rivers dissolves salt from the soils and rocks on the land and carries this salt to the ocean, where it accumulates. To this it is answered that, as a matter of fact, in rocks and soils potassium salts are more abundant than sodium salts. It is true, it may be said, that sodium minerals are more easily decomposed; and that, therefore, sodium salts go into solution more quickly than potassium salts.

Some chemists prefer to believe that the salt of the ocean is a part of the original chloride of sodium formed at the time of the cooling of the earth from the state of vapor to the state of solid. In this view the geologic primeval rains dissolved the chloride of sodium and quickly carried it to hollow places in the earth, where it has ever since remained. Even this explanation, however, is not entirely satisfactory.

— Common salt exists as deposits of brine under the surface of the earth. (The water of many mineral springs, those of Saratoga, for instance, contains more sodium chloride than other mineral salts.)

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* Dittmar: Report on composition of ocean water, *Challenger* Expedition, 1884.

— Common salt exists in certain salt lakes like the Dead Sea and the Great Salt Lake in Utah.

— Common salt exists in smaller quantities in most natural waters, even so-called fresh waters of rivers, lakes, etc.

Fig. 6. Mine of rock salt at Bochnia, in Galicia (Carpathian Mountains.)

Preparation of sodium chloride. — Sodium chloride may be prepared artificially by direct action of chlorine gas upon metallic sodium ; also by many processes of double decomposition of chemical salts. Thus the interaction of a solution of barium chloride and a solution of sodium sulphate gives rise to the production of sodium chloride and barium sulphate :

$$BaCl_2 \quad + \quad Na_2SO_4 \quad = \quad 2NaCl \quad + \quad BaSO_4$$

— Sodium chloride is usually obtained from natural sources. Thus it is mined as a solid. But the solid is usually subjected to processes of purification. Sometimes a shaft is bored into the solid deposit. Water is then allowed to run down the shaft and to dissolve the salt. The brine so produced is pumped to the surface ; it is afterwards evaporated for the purpose of securing the solid salt.

— Sea water is often evaporated so as to produce common salt.

In tropical regions, sea water is run into large reservoirs or lagoons, near the coast, and the heat of the sun is utilized. Solar evaporation is also practiced in some temperate regions. Here the reservoirs are often provided with sliding roofs, which may be removed in fine weather, but put in place during rain.

— The water of natural brine springs is often pumped to the surface and evaporated. In some parts of Germany evaporation is partially accomplished by use of the "graduation house." This is a structure having two tanks, one on the

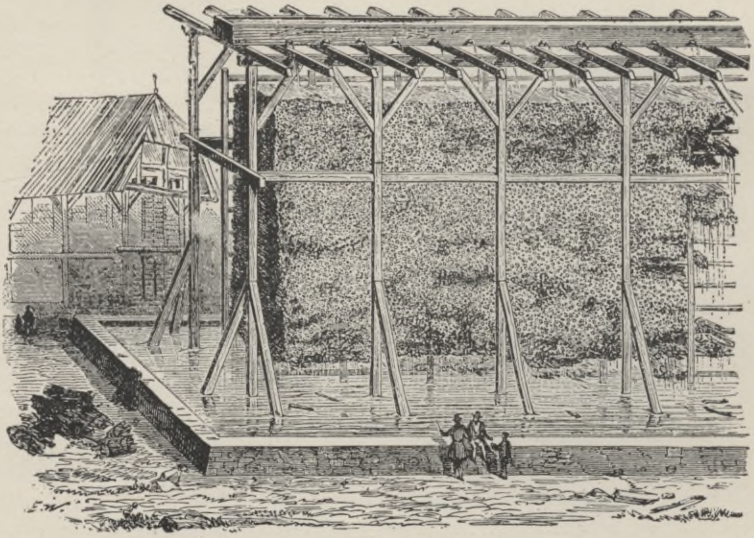

Fig. 7. "Graduation house." Natural brine, from a well, is pumped into the upper tank. It is allowed to trickle over the fagots. By the time it reaches the lower tank it concentrates, losing water by natural evaporation.

ground and one high in the air. Between them a wall of fagots is erected. The brine is pumped into the upper tank, then allowed to trickle over the fagots toward the lower tank. In its progress a large surface of water is exposed to the winds under conditions favorable for abundant evaporation. When the brine in the lower tank is nearly ready to crystallize, the operation is completed in pans heated by the use of fuel.

In the production of salt from brine, the question of evaporation is an important one. Owing to the high specific heat of water and its high latent heat of evaporation, the cost of fuel for evaporation is very great. Every effort is made towards saving in this direction.

— Salt is produced from the water of the Great Salt Lake.

This lake is evidently the shrunken remnant of a vast interior sea. A recent investigation shows that the total solid matter dissolved in the water amounts to between fifteen and twenty per cent. The waters of the lake rise and fall, become more concentrated or more dilute, according as supply of fresh water — or evaporation — varies. Two or three consecutive winters with heavy snows, dilute the water in a marked degree.*

The following table presents an analysis of the solid matters in this water in August, 1889:

	Grammes per litre.	Per cent. by weight.
Sodium chloride, $NaCl$	182.131	15.7430
Sodium sulphate, Na_2SO_4	12.150	1.0502
Magnesium chloride, $MgCl_2$	23.270	2.0114
Calcium sulphate, $CaSO_4$	3.225	.2788
Potassium sulphate, K_2SO_4	5.487	.4742
Total solids	226.263	19.5576

The manufacture of salt from the water of the Great Salt Lake is carried on on a large scale. Two general methods are pursued. At some of the greater works, evaporating ponds are constructed adjacent to the lake and a little *below* its

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* For the tables and information presented here, acknowledgment is made to James E. Talmage, who publishes an interesting account of this subject in *Science* for Dec. 27, 1889.

level. The water being run into these ponds, the natural evaporation reduces the brine to dryness, when an abundant mass of salt is obtained. Of course it is somewhat impure.

At other works ponds are constructed *above* the level of the lake. These are arranged and managed on a more elaborate scale and by a more scientific method than those just referred to.

In a given case the system may cover some thousands of acres, divided into as many as nine separate reservoirs. During the months of May, June, and July, the water of the lake is pumped through a pipe-line to the first pond. Thence it flows by a sort of decanting process to the others in succession. During the summer months evaporation proceeds rapidly. Above eight million gallons of water pass into the air daily in this way from a single establishment. When the salt has crystallized to the proper extent, the mother liquors, containing other materials than chloride of sodium, are allowed to flow back into the lake. The salt harvest begins in August. A layer of salt seven inches in depth is formed. It is subsequently scraped up and sent to market.

As the analysis shows, large quantities of sodium sulphate exist in the waters of the lake. Under certain conditions of temperature in winter, this substance crystallizes out of the water in the form of opalescent powder, but much of it is carried by the waters of the lake up upon the beach It is there deposited as white masses. It has been proposed to utilize this natural sodium sulphate for the production of sodium carbonate and caustic soda by the Leblanc method.

Properties of sodium chloride. — Sodium chloride is well known as a white solid, easily soluble in water, and possessing a characteristic taste. Under certain conditions it easily crystallizes in cubical crystals. Often, when these form on the surface of a solution, they produce hopper-shaped masses. A single crystal sinks a little from the surface, and then other crystals form about the four upper edges. Thus a hopper is produced. Later, it enlarges by addition of other crystals, in a manner similar to that described.

Crystals of sodium chloride are highly diathermanous. That is, the substance permits heat-rays, both luminous and non-luminous, to pass through, only a very small percentage of them being retained by the solid.

Sodium chloride is easily melted, and even vaporized, by heating.

The solubility of sodium chloride in water does not increase rapidly, as the temperature of the liquid rises. Thus, at 14° C., 100 parts of water dissolve 35.87 parts sodium chloride ; at 100° C., they dissolve only 39.16 parts.

Under ordinary conditions of preparation, common salt crystallizes without water of crystallization, but from very cold brine two definite hydrates, $NaCl \cdot 2H_2O$, and $NaCl \cdot 10H_2O$, may be formed.

Uses of sodium chloride. — 1. Common salt is used directly as an article of food; again, vast quantities of it are used in the preservation of certain forms of food, as meats and fish.

2. Common salt is used in enormous amounts in certain chemical industries, especially in the alkali trade, the largest strictly chemical trade conducted by man. Common salt constitutes man's chief source of *chlorine* and his most practicable source of *sodium;* hence virtually all chlorides and all sodium salts are made, directly or indirectly, from common salt.

Of the amount of salt consumed in the United States, Michigan furnishes approximately one-third, New York one-fourth, other States one-sixth. About one-fourth is imported (partly as ballast).

Sodium Monoxide, Na_2O.

This oxide may be formed by a variety of processes:

— The ordinary burning of metallic sodium in dry oxygen or air, proceeds as described by the equation:

$$2Na_2 \quad + \quad O_2 \quad = \quad 2Na_2O$$

— The action of metallic sodium upon sodium hydroxide proceeds as described by the equation:

$$2NaOH \quad + \quad Na_2 \quad = \quad 2Na_2O \quad + \quad H_2$$

— When metallic sodium is thrown upon hot water (or is kept in one place upon the surface of cold water), a portion of the sodium burns in the air into sodium monoxide (but the larger portion reacts with the water forming sodium hydroxide):

$$Na_2 \quad + \quad 2H_2O \quad = \quad 2NaOH \quad + \quad H_2$$

The sodium hydroxide may be viewed as formed by the action of sodium oxide upon water; and this change may in fact be realized:

$$Na_2O \quad + \quad H_2O \quad = \quad 2NaOH$$

Sodium Hydroxide, NaOH (Caustic Soda).

Sodium hydroxide, NaOH, is called *caustic soda,* and this latter name is extended to combinations of sodium hydroxide (some of them solid and some liquid) with more water. In commerce several grades of solid caustic soda, having various quantities of combined water, are sold under the name caustic soda, or simply "caustic."

This substance is now one of the important products of the alkali trade.

It is manufactured as follows:

1st. To a solution of sodium carbonate, milk of lime is added; sodium hydroxide is formed (it dissolves in the water present); calcium carbonate is formed (it separates as a white precipitate):

$$Na_2CO_3 \quad + \quad CaO_2H_2 \quad = \quad CaCO_3 \quad + \quad 2NaOH$$

2d. A water solution of sodium chloride is electrolyzed: chlorine is liberated as a gas and sodium hydroxide is dissolved in the water present.

In either case, the dilute solution of caustic soda is boiled down in iron kettles until almost all of the water is expelled. The hot liquid left is ladled into steel drums, in which it solidifies upon cooling. The drums are then sealed so as to prevent access of air.

Caustic soda is largely used in commerce in the manufacture of soap, in bleaching of cotton cloth, in the manufacture of wood paper (called "pulp"), and in a great many chemical industries.

Sodium Peroxide, Na_2O_2.

This substance is now prepared by Castner's process, on a large scale by oxidizing metallic sodium in a special furnace. The furnace has a long, tube-like oven which may be heated to a fixed temperature. The metallic sodium, placed, in weighed quantities in suitable dishes, is made to advance steadily through the tube-like oven: at the same time, dried air passes in a current through the oven. When the dishes complete their trip through the oven, the sodium is oxidized to peroxide.

The substance is a dry, white powder. When it is placed in water or aqueous liquids, it develops considerable heat, and it decomposes as follows:

$$Na_2O_2 \quad + \quad 2H_2O \quad = \quad 2NaOH \quad + \quad H_2O_2$$

It may even set on fire moist vegetable and animal matters with which any considerable quantity of it may come in contact. If exposed to the air, it absorbs carbon dioxide, forming sodium carbonate, Na_2CO_3, and liberating oxygen gas.

This substance is used for producing hydrogen dioxide, H_2O_2.

It is also a valuable bleaching agent, and it is used as such upon a great variety of animal and vegetable textile fabrics. Such goods are first thoroughly washed and cleansed from adhering dirt and from natural gums, etc., an alkaline solution being used. Next they are immersed in a bath containing dilute sulphuric acid or some mild acid like oxalic acid. The sodium peroxide is powdered in carefully, the bath being thoroughly stirred. Active oxygen is liberated and it accomplishes the bleaching.

Sodium Sulphate, Na_2SO_4.

This substance (often called Glauber's salt) is found in some parts of the earth ready-formed.

It is produced in large quantities as a by-product, in certain manufacturing operations, namely: in all those where sulphuric acid is added to sodium salts.

Thus great quantities are produced in a crude form called *salt-cake*, in one stage of the Leblanc process of making soda-ash. This stage corresponds strictly to the manufacture of hydrochloric acid by adding sulphuric acid to common salt.

A similar sodium sulphate is also produced in the manufacture of nitric acid, by the addition of sulphuric acid to Chile saltpetre, sodium nitrate, $NaNO_3$. This form is called *nitre-cake*.

The compound is a white solid. It is capable of combining, under different circumstances, with different amounts of water of crystallization; thus it forms:

$$Na_2SO_4, \quad \text{also } Na_2SO_4 \cdot 7H_2O, \quad \text{also } Na_2SO_4 \cdot 10H_2O.$$

It is used to a considerable extent in the manufacture of glass; here it so reacts with sand (silicic anhydride, SiO_2) as to form a sodium silicate.

Sodium Tetraborate (Borax.)

A considerable number of borates of sodium are known, but borax is the most important one. It is used either in the form of crystals or powdered crystals having the formula, $Na_2B_4O_7 \cdot 10H_2O$.

Borax is a derivative of boron trioxide, B_2O_3; this substance is an acid anhydride. It forms three well-marked acids: orthoboric acid, H_3BO_3; metaboric acid, $H_2B_2O_4$; pyroboric acid, $H_2B_4O_7$. These acids yield, in turn a large number of metallic salts — orthoborates, metaborates, and pyroborates, respectively.

The manufacture of borax depends upon the securing of natural compounds of boron. The principal natural sources of such compounds are mentioned below:

First. — In certain parts of Tuscany there exist natural crevices in the earth called *soffioni* or fumaroles, from which steam escapes. As early as 1776 it was discovered that this steam contains traces of boric acid (about $\frac{1}{10}$ per cent).*

Second. — In Tuscany, near Sasso, occur natural deposits of a crude boric acid in the solid form called *sassolite*, H_3BO_3.

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* See Appleton's Chemistry of the Non-metals, p. 108.

Third.—In San Bernardino County, Southern California, boric deposits have been discovered in the form of a vein uplifted from its original position. The exact material is a kind of borate of lime (containing anhydrous boric acid) called *colemanite.* This particular deposit is said to be six feet thick and otherwise of great extent.

Fourth.—On the plains of Iquique, Equador, are found deposits of a mineral called *boronatrocalcite*, or *ulexite*, $Ca_2B_6O_{11} \cdot Na_2B_4O_7 \cdot 16H_2O$.

Fifth.—In the west central part of Nevada, calcium borate is found as a solid mineral.

Sixth.—In the mountains of Thibet ready formed borax is found as a solid mineral called *tincal.*

Seventh.—In the northern part of California (near Clear Lake, about 39° N., 123° W.) in the waters of Borax Lake, borax occurs dissolved in the water. Moreover, in the mud at the bottom of this Lake crystalized borax occurs; it is secured by the use of water-tight caissons.

The chief supplies of borax of the world are derived from the Tuscan sources, and from the Pacific States of North America.*

In the preparation of borax the mineral borates may in some cases be boiled directly with soda-ash, Na_2CO_3. In other cases the mineral may be first decomposed with hydrochloric acid; as a result boric acid separates as white, pearly flakes. Such flakes (as well as naturally occurring boric acid) are subsequently transferred to tanks of water, heated by steam, containing dissolved soda-ash. Sodium borate is formed; it is afterwards crystallized as borax.

Borax is a white solid, easily soluble in water. It has mild alkaline tendencies; whence it is suited for detergent uses. It is mildly astringent; whence it is suitable for medical use.

Borax has many uses. Since the discovery of borax in the Pacific States of North America, the production and consumption of the article have very much increased.

It is largely used in certain metallurgical operations on copper, the welding of iron or steel, the enameling of metallic vessels, as a fire-proof lining between the shelves of safes.

Mixed with other substances, it is used to produce fusible glass for use in the ceramic arts.

As a solvent for shellac and other similar matter, it is employed in the manufacture of hats, and the cleansing of raw silk.

As a neutral substance and a non-combustible and fusible one, it is employed in fire-proofing delicate fabrics of linen, paper, etc.

It is used in candle-wicks to make the burning cease when the candle is extinguished.

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* *Chemical News*, 63.74, also 54.244.

It is used in the leather industry as a tanning material, and in connection with dyeing operations.

A great many forms of food are rendered antiseptic by the use of borax or boric acid.

It is used in medicine as an astringent (as is also boric acid).

It is used in washing operations as a mildly alkaline substance.

Sodium Nitrate, $NaNO_3$.

This substance, called Chile saltpetre, is a very important article of commerce.

It is found as a solid in abundant deposits in Chile and Peru.

It is subjected to purification by dissolving in water and recrystallizing.

It is a white salt; very easily soluble in water; somewhat deliquescent (whence it cannot be used in gunpowder). It is man's chief source from which are derived *oxidized* compounds of nitrogen.

It is used in enormous quantity:

—In the manufacture of nitric acid,*
—In the manufacture of sulphuric acid,*
—In agriculture, as a source of nitrogen for fertilizers,*
—In the manufacture of other nitrates, especially of potassium nitrate.

Sodium Carbonates.

Many different carbonates of sodium are known. The following list comprises those of chief importance:

Sodium carbonate,	called	soda-ash,	Na_2CO_3
——	"	monohydrate crystals,	$Na_2CO_3 \cdot H_2O$
——		——	$Na_2CO_3 \cdot 5H_2O$
——		——	$Na_2CO_3 \cdot 6H_2O$
——		——	$Na_2CO_3 \cdot 7H_2O$
——	"	sal soda or soda crystals,	$Na_2CO_3 \cdot 10H_2O$
——		——	$Na_2CO_3 \cdot 15H_2O$
Hydrosodium carbonate,	"	bicarbonate of soda,	$HNaCO_3$
Sodium sesquicarbonate,	"	snowflake crystals,	$Na_2CO \cdot HNaCO_3 \cdot 2H_2O$
——		——	$Na_2CO_3 \cdot 2(HNaCO^3) \cdot 3H_2O$

Of the substances mentioned, soda-ash and bicarbonate of soda are commercially the most important. Monohydrate crystals, sal soda and snowflake crystals have a moderate importance; most of the others in the list are, at present, of interest to the chemist only.

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* See Appleton's Chemistry of the Non-metals, pp. 127; 97; 133.

Soda-ash, Na_2CO_3.

This is probably the most important chemical product made by man.

It is manufactured on an enormous scale in each of the great industrial countries of the world.

While it exists ready-formed in certain arid regions it is rarely prepared from natural deposits. The commercial supply is derived exclusively from common salt. The preparation of soda-ash is described, at length, later (commencing at p. 45).

Soda-ash, when pure, is a white solid, easily soluble in water. It has mild alkaline properties ; it neutralizes most acids, forming sodium salts of those acids, with simultaneous liberation of gaseous carbon dioxide from the soda-ash.

The uses of soda-ash are very various ; a multitude of different industries employ it directly or indirectly. It is directly used in the manufacture of glass and in the bleaching of cotton, woolen, and silk goods. It is indirectly used in the manufacture of soap (the soda-ash being first causticised, *i. e.*, changed to sodium hydroxide, $NaOH$. See p. 37.) Moreover many of the industries demanding it, employ it in very large quantities.

Sal Soda ; Monohydrate Crystals.

These substances differ from soda-ash only in the fact that they contain water of crystallization (as shown already).

They are produced by dissolving soda-ash in water and then crystallizing a product from this solution. Now the kind of product obtained depends mainly upon the conditions under which the crystallization occurs — in the case, as in others, crystallization at the higher temperatures gives rise to crystals having the smaller amounts of water of crystallization, while crystallization at lower temperatures gives rise to crystals having the larger amounts of water of crystallization.*

Hydrosodium Carbonate, $HNaCO_3$.

This substance, commonly called bicarbonate of soda, is an artificial product.

— It may be formed when moisture and carbon dioxide gas are passed over soda-ash at moderate temperatures :

$$Na_2CO_3 \quad + \quad H_2O \quad + \quad CO_2 \quad = \quad 2HNaCO_3$$

— It has long been customary to produce it by passing carbon dioxide gas into a mass of sal soda crystals :

$$Na_2CO_3 \cdot 10H_2O \quad + \quad CO_2 \quad = \quad 2HNaCO_3 \quad + \quad 9H_2O$$

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* Appleton's Chemical Philosophy, pp. 126, 127.

(In this case, the water of crystallization furnishes the necessary moisture; but the expelled water introduces a difficulty: it dissolves a portion of sodium carbonate, which has to be subsequently recovered.)

— In the manufacture of soda-ash by the ammonia process (see p. 51) hydrosodium carbonate is produced in enormous quantities. (But it contains certain objectionable impurities, viz., sodium chloride, ammonium chloride, ammonium carbonate, and others) It may be purified by redissolving the crude hydrosodium carbonate in water, and subsequently recrystallizing it.

The salt is a white powder which, when heated, easily changes to soda-ash — losing one molecule of carbon dioxide and one molecule of water.

The chief use of bicarbonate of soda is in the manufacture of baking powders. These baking powders usually contain bicarbonate of soda, a solid acid-tartrate of potassium (called cream of tartar), and starch. (Sometimes solid acid phosphate of calcium is used in place of the cream of tartar.) So long as the powder is kept dry the substances do not react with each other. When, however, the powder is mixed with water, in the process of making bread or other articles of food, the carbonate and the acid salt are at once dissolved and then reacting they give rise to an evolution of carbon dioxide gas. It is this gas in the form of minute bubbles, distributed throughout the dough, that makes the latter light and porous.

Sodium Silicates.

It must be recognized at the outset that certain natural obstacles make it difficult to secure knowledge as to the exact molecular composition of silicates. Among these are the great number and complexity of these compounds known, and the non-volatility of them.

Many silicates are known which are clearly either mixtures of silicates of two or more metals at once, or else are mixtures of two or more silicates of the same metal. Thus glass is a complex mixture of silicates: generally it contains a silicate of sodium interfused, or else chemically combined, with silicates of other metals. Again, many artificial silicates of sodium, without any other metal, are producible; in a given case it is difficult to determine whether such a sodium silicate is a definite single compound, or is an interfused mixture of two or more different but definite sodium silicates. And further, such a compound as that represented by the expression $Na_2Si_4O_9$ may consist of definite molecules as just represented or it may be a mixture more properly represented by the expression $Na_2SiO_3 \cdot 3SiO_2$.

Chemists have formed sodium silicates that are practically insoluble in water, and also those that are completely soluble in water — the latter often known as soluble glass.

Such compounds are produced by fusing some form of silicon dioxide (as powdered quartz or infusorial earth) with sodium carbonate, or else by boiling some form of silicon dioxide with sodium hydroxide.

The soluble sodium silicates produced are not very stable: they are easily decomposed by a variety of chemical agents and operations.

Soluble sodium silicates are considerably used as mild alkaline agents in calico-printing: they are also mixed with soap as cheaper substitutes for rosin.

First Appendix to Sodium.—The Alkali Trade.

The term "alkali trade" is applied, especially in England, to the industry or the congeries of industries whose chief product is soda-ash, sodium carbonate, Na_2CO_3. As now conducted, this industry often involves the production of caustic soda, (sodium hydroxide, NaOH); bleaching powder; sulphuric acid; and in smaller quantities more than a dozen other substances. It is reckoned as the greatest distinctly chemical industry conducted by man.

The word alkali in its narrowest chemical sense applies to three substances, sodium hydroxide, NaOH; potassium hydroxide, KOH; ammonium hydroxide, NH_4OH. Perhaps the chief properties common to these substances, and upon which the definition is based, are solubility in water, power of turning vegetable colors like litmus from red to blue, power of neutralizing acids to form salts.

The word alkali is often used in a wider sense in chemistry to include sodium carbonate, Na_2CO_3; potassium carbonate, K_2CO_3; ammonium carbonate, $(NH_4)_2CO_3$; but these are more exactly spoken of as alkaline carbonates.

The word "alkali" is used in English trade, in a very narrow sense: to designate soda-ash of a special standard strength; viz., that which has an amount of sodium carbonate equivalent to about 48 per cent. of sodium oxide, Na_2O.

Sodium Carbonate in Nature.

Sodium carbonate occurs to a limited extent ready-formed in nature.

It occurs in the water of certain mineral springs; it occurs in certain so-called natron-lakes in Hungary, Egypt, Africa, North America. When in dry seasons, ponds of such water evaporate considerably, solid deposits of sodium carbonate, in a more or less white condition, are formed.

In Egypt, it has long been the practice to use deposits formed somewhat as above described. In the United States there are extensive stretches of territory called alkali plains. There are white alkali soils (in which sodium sulphate predominates), and black alkali soils (in which sodium carbonate predominates).

Artificial Production of Soda-ash.

The alkali trade may be discussed as having progressed through three periods — a fourth period is now impending.

The first period is the ancient one : a crude sodium carbonate was produced from the ashes of marine plants. *The second period* is that of the Leblanc process: by this process sodium carbonate is produced, by a special series of operations, from common salt. *The third period* is that of the ammonia-soda process : common salt is the starting point of this process also. Both the Leblanc process and the ammonia-soda process are now carried on on an enormous scale. *The fourth period* is that of the electrolytic processes : common salt is electrolyzed so as to yield at once chlorine gas and sodium hydroxide (caustic soda) — but not soda-ash.

First. — The Ancient Process.

It has long been customary to collect sea-weeds, and also plants growing in the water of the ocean's margin, and then to dry and burn them. Thus, along the coasts of Great Britain, France, and especially of Spain, sea-weed of various kinds was gathered as a very important harvest. Some of the weed was used as a fertilizer of the soil ; more was dried and burned for the sake of the ashes. On the British coast the ash was known as *kelp ;* that produced on the coasts of Normandy was called *varech ;* and that produced on the Spanish coast went by the name of *barilla.*

The ashes contain, among other substances, sodium carbonate.

Growing land plants generally exercise an important selective influence upon the mineral matters of the soil in which they grow ; i. e., while the soil usually contains less of potassium compounds than of sodium compounds, the ashes of land plants usually contain more of potassium compounds (varying from the equivalent of 3 per cent. to 46 per cent. K_2O) than of sodium compounds.

Marine plants exert a similar selective action, varying very much, however, with the kind of plant and its habitat. (The ocean contains sodium compounds vastly greater in amount than potassium compounds. See p. 32.)

(*a*) In case of certain marine plants, especially those growing on or near the shore, the ashes contain sodium compounds to the almost entire exclusion of potassium compounds.

Such ashes may contain so much as 60 per cent. to 70 per cent. of sodium chloride, and so much as 25 per cent. to 30 per cent. of sodium sulphite, and so little as 2 per cent. of sodium carbonate. In other cases, sodium carbonate may be present to the extent of 30 per cent. to 46 per cent.

On the coasts of Spain, planting with selected seed is carried on with such success as to secure plants whose ashes uniformly yield the larger proportions not only of sodium compounds in general, but of sodium carbonate in particular.

(*b*) Sea-weed from the deep water of the ocean contains relatively larger proportions of potassium compounds (and also of iodides). In such cases the ashes may contain as much as 16 per cent. of potassium chloride plus as much as 22 per cent. of potassium sulphate (although at the same time abundance of sodium compounds, especially sodium chloride, are always present).

Up to about 1793, such ashes were employed in Europe as the principal source of the alkali employed in the manufacture of soap and of glass and in other operations. Since the date mentioned, sea-weed ashes have been used with the view of obtaining iodine as a chief product.

The French Revolution and the Napoleonic wars following it, involving England, France, and Spain, as well as the other countries of Europe, had an influence on the industry now under consideration.

As early as 1795 the French Committee of Public Safety had considered the possibility of excluding English products from the Continent. For several years, Napoleon was occupied with a similar idea. The English embargo of May 18, 1803, the British Order in Council of Aug. 17, 1805, Napoleon's Prussian Decree of 1806, the British Orders in Council of May 16, 1806, Napoleon's Berlin Decrees of Nov. 21, 1806, the Orders in Council of Nov 11, 1807, Napoleon's Milan Decree of Dec. 17, 1807, all seriously disturbed the European commerce of the time. To a considerable extent they interfered with the introduction of foreign alkaline ashes, such as kelp and barilla, into France. But the French demand for alkali from sea-weed — that is, sodic alkali — was very much stimulated by the draft upon the potassic alkali for the preparation of the great amounts of saltpetre required for the manufacture of gunpowder.

As a result, the French chemists pressed with the greater vigor, attempts previously made to produce soda-ash (sodium carbonate) from common salt. Many different methods were proposed. All were relatively complex — considering the chemical skill of the period. The Leblanc process at length prevailed.

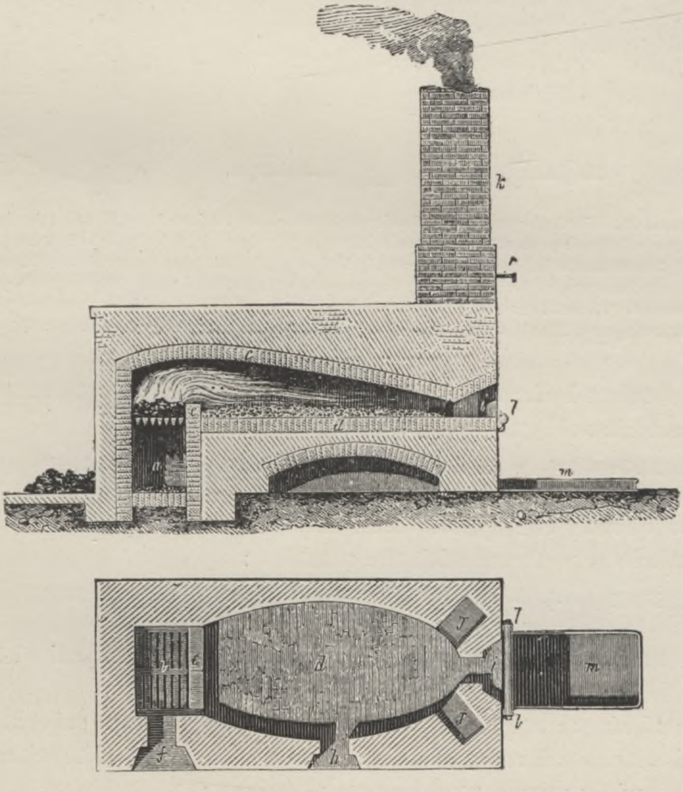
Second — The Leblanc Process.

This process was devised by a French chemist, Nicholas Leblanc, about 1787. In plan, it was ingenious and logical; but its inventor experienced such political and financial difficulties that it was slow in gaining a foothold as a practical industrial method. It was first successfully carried out on a large commercial scale, in 1824, by James Muspratt, in England. Since this demonstration of its practicability as a regular working process, details have been studied, by-products utilized (in the works or out of them) apparatus has been improved (made more automatic, larger, and more effective), new plants have been constructed, a more strict chemical "control" has been effected, the scope of the business has been widened, until it has become the greatest chemical industry in the world.

The Leblanc process as now conducted may be described as conducted in four principal departments:

The First Department. — The manufacture of sulphuric acid. This has been described elsewhere.*

The Second Department. — The manufacture of soda-ash. The *salt-cake* stage is that in which sulphuric acid is added to common



Figs. 8 and 9. **Vertical section and horizontal section of French Leblanc black-ash furnace.** The proper mixture ot salt-cake, coal, and limestone is heated in this furnace. It produces black ash, which is raked out into the pan *m*. Subsequently the black-ash is lixiviated with water to produce soda-ash.

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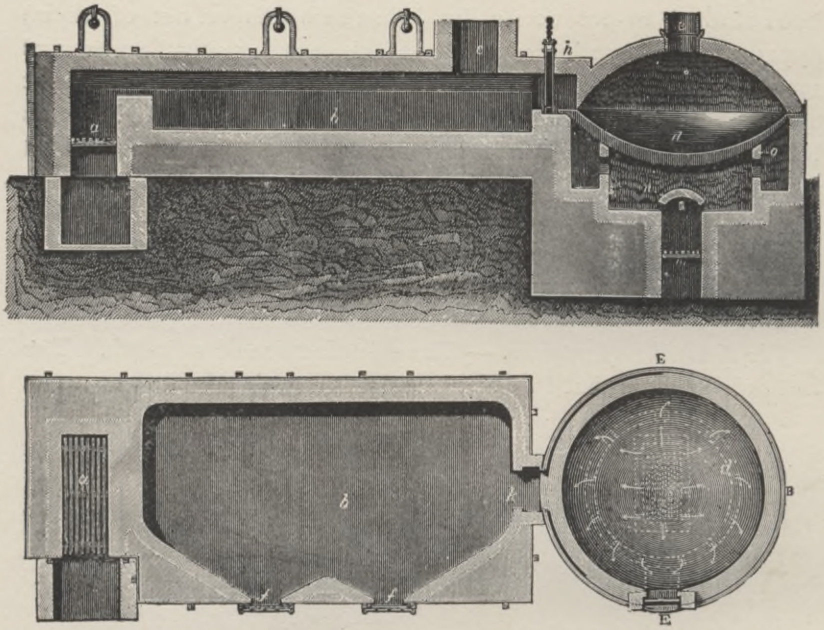
* Appleton's Chemistry of the Non-metals, p. 96.



Figs. 10 and 11. Vertical section and horizontal section of modern English salt-cake furnace (for use in Leblanc process). Common salt and sulphuric acid are introduced into the pan at the right: salt-cake is formed in the pan *d*; hydrochloric acid gas escapes through the large pipe over the centre of the pan. Later the salt-cake is transferred to the large adjoining compartment *b*. Here it is roasted; more hydrochloric gas escapes through a separate pipe *c*. (This arrangement has the advantage of separating "pan-gas" from "roaster-gas.")

salt. At first hydrosodium sulphate is produced and torrents of hydrochloric acid gas are liberated:

$$NaCl + H_2SO_4 = HNaSO_4 + HCl$$

Subsequently the hydrosodium sulphate reacts upon more common salt in accordance with the reaction:

$$NaCl + HNaSO_4 = Na_2SO_4 + HCl$$

The sodium sulphate produced by this operation is called salt-cake.

The *black ash stage* is that in which the sodium sulphate is heated with powdered coal and limestone, $CaCO_3$. The changes may be rudely represented by two reactions:

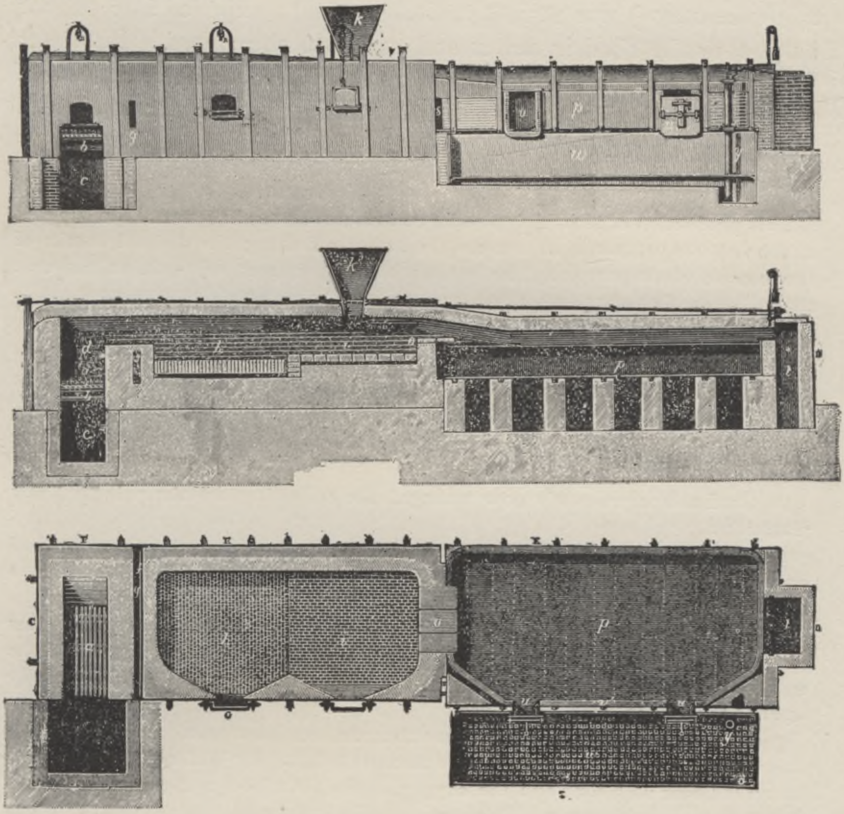
$$Na_2SO_4 + C_4 = Na_2S + 4CO$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

As a matter of fact the two operations proceed at once; moreover, certain other substances are formed.

But the solid mass produced is called black-ash.

The *lixiviation stage* is that in which the black-ash (a mixture containing approximately 44 per cent. of sodium carbonate and 31 per cent. of calcium sulphide) is treated with water to dissolve the sodium carbonate. (An undissolved portion — alkali waste — is left.)

The liquid obtained is evaporated and the product roasted, to produce soda-ash.



Figs. 12, 13, 14. **Front elevation, vertical section and horizontal section of English black-ash furnace.** The fire-place is at the left; its flames draw through the furnace to the chimney flue (leading downward) at the extreme right. At the left centre are the furnace beds; at the right of them the boiling down pan *p*; in front of the pan a drainer. The mixture of salt-cake, limestone, and coal is introduced through the hopper; it is heated and worked first in one furnace-bed, then in the other. The pan *p*, is used for evaporation of the solution of soda-ash (thus utilizing waste-heat of the furnace): when this latter operation is nearly complete, the pasty material may be drawn out upon the drainer.

The solid residue, called "alkali-waste," consists of calcium compounds some of which are rich in sulphur. For many years these have created a great nuisance in the neighborhood of alkali works. They have formed heaps, like small mountains, which have given off sulphuretted hydrogen, a substance of unpleasant odor and unwholesome. When the rain fell upon them it produced a trickling of foul and polluting liquids into the adjacent rivers. (At present, Chance's process successfully overcomes this nuisance. It profitably extracts the sulphur — the chief cause of offense — producing sulphur for sale or else for renewed manufacture of sulphuric acid.)*

The Third Department. — The manufacture of bleaching powder. The hydrochloric acid above referred to (second department, salt-cake stage) was at first entirely wasted: expelled into the air as gas, or absorbed in water and run into the rivers. But later Tennant, a Scotch manufacturer, used this hydrochloric acid upon manganese dioxide to generate chlorine, and he absorbed the chlorine in slaked lime, calcium hydroxide, CaO_2H_2, and thus produced bleaching powder.

This production of bleaching powder contributes somewhat toward the support of the Leblanc process, thus to a certain extent offsetting the decided merits of the ammonia-soda process. The latter, while it produces soda-ash at less cost than does the Leblanc process, produces practically no bleaching powder at all.

The Fourth Department. — The manufacture of caustic soda. In this department caustic soda (sodium hydroxide), NaOH, is made from soda-ash by use of calcium hydroxide. (It has been described already at p. 38.)

As the Leblanc process is now managed the following are the principal raw materials:

1 — Common salt, NaCl. Practically all the sodium goes into the finished products, soda-ash and caustic soda. About one-half of the chlorine goes into bleaching powder; about one-half is finally thrown away as calcium chloride.

2 — Sicily sulphur, or Spanish pyrites. These are oxidized to produce sulphur dioxide, which in turn is changed into sulphuric acid. Moreover, most of the sulphur is recovered by Chance's process. The ashes of the pyrites are carefully worked for copper, gold, and silver.

3 — Manganese dioxide. After the substance has been acted upon by hydrochloric acid, a solution of manganous chloride is left. By Weldon's process, this is worked over with lime and the oxygen of the air. Manganese dioxide is produced for subsequent use. Calcium chloride is formed, but the most of it has to be thrown away.

4 — Limestone, $CaCO_3$. Of the carbon dioxide derived from this substance a considerable part goes into the finished product, the soda-ash. But a large part

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* Appleton's Chemistry of the Non-metals, p. 91.

of it combines with calcium either in the causticising process or else in Chance's sulphur recovery process, and is thrown away as calcium carbonate. A part of the calcium oxide produced goes into the finished product, bleaching powder. A large portion, however, is thrown away as calcium carbonate (referred to in the opening lines of this paragraph), or as calcium chloride, incidental to the Weldon manganese recovery process.

5 — Coal and coke. A part is used in the black-ash process (as above); a part is used as fuel in the lime kilns or elsewhere.

The principal commercial products of the Leblanc works are:

1 — Sulphuric acid, H_2SO_4,
2 — Sulphur,
3 — Copper, gold, silver (in relatively small quantity),
4 — Salt-cake (some of this is refined to Glauber's salt, Na_2SO_4),
5 — Hydrochloric acid, HCl,
6 — Bleaching powder, $CaCl_2O_2 \cdot CaCl_2 \cdot CaO_2H_2$,
7 — Soda-ash, Na_2CO_3,
8 — Soda crystals, Na_2CO_3, $10H_2O$,
9 — Monohydrate crystals, Na_2CO_3, H_2O,
10 — Bicarbonate of soda, $HNaCO_3$,
11 — Caustic soda, $NaOH$,
12 — Calcium chloride, $CaCl_2$ (only small quantities are sold),
13 — Calcium carbonate, $CaCO_3$. This is a product of the causticising operation. Some of it goes to waste. Some of it is used as a "filling" in paper.

The waste products are:

1 — Alkali waste (highly sulphuretted calcium compounds). Of late, this waste is largely done away with by Chance's sulphur recovery process.

2 — Calcium chloride, $CaCl_2$. This appears to be an unavoidable waste material. Small quantities are sold for use as a cooling brine in ice-making or in cold storage houses; but the total quantity of calcium chloride produced is so great, that the most of it has to be thrown away (though great efforts have been made to utilize it).

Third—The Ammonia-Soda Process.

This process was invented by two Englishmen, Dyar and Hemming, as early as 1838. But it was first made a commercial success (about 1863) by the engineering skill of two Belgians, Ernest Solvay and Alfred Solvay, brothers. They invented a variety of pieces of apparatus which were admirably adapted for the work. Moreover they devised the plan of establishing plants in the principal industrial countries — plants which should be worked in a common interest.

It is said that the amount of soda-ash now made in the world, practically by Solvay methods, is equivalent to one ton of ash for every minute, night and day, of the year.

The First Department. — The manufacture of soda-ash. The operations of this department may be outlined as follows :

First principal process. Common salt is dissolved in water (the natural brine of suitable salt wells is generally used). To this brine, ammonia gas is added in suitable quantity.

Second principal process. The ammoniated brine is transferred to large iron tanks, cylindrical in form, called "towers." The towers contain many umbrella-shaped perforated diaphragms. Now a stream of carbonic gas is forced by pumps through the ammoniacal brine in the towers. A white precipitate of hydrosodium carbonate, $HNaCO_3$, quickly forms :

$$NaCl + NH_4OH + CO_2 = HNaCO_3 + NH_4Cl$$

Third principal process. The tower liquid is filtered in large tubs supplied with strainers lined with cloth. The filtering is quickened by aid of suction pumps. The hydrosodium carbonate remains as a white solid in the tubs. The ammonium chloride passes away in solution ; it goes to the recovery apparatus (second subordinate process).

Fourth principal process. The hydrosodium carbonate is transferred to large roasting furnaces. In these the compound is decomposed :

$$2HNaCO_3 \text{ heated } = Na_2CO_3 + H_2O + CO_2$$

Soda-ash is formed and it remains in the furnaces. Carbonic gas is liberated ; it is caught by a dome shaped cover and it is pumped away for use in the towers. (With it goes off a certain amount of ammonia gas which, as ammonium compounds, adheres to the solid bicarbonate on the filters. This ammonia gas is also saved.)

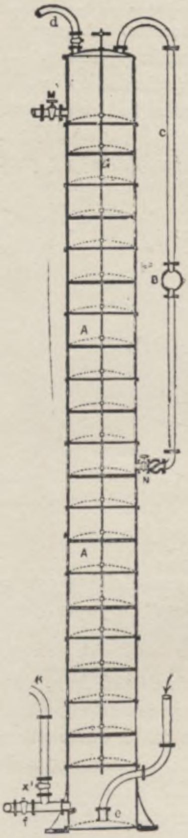

Fig. 15. Section of Solvay tower for carbonating brine in the ammonia-soda process. The carbonic gas passes into the tower by the right-hand lower pipe. It is thoroughly distributed by the perforated diaphragms.

First subordinate process. Coke is burned in a kiln, and then limestone, mixed with more coke, is added. The coke affords carbon dioxide :

$$C + O_2 + CO_2$$

The limestone is decomposed:

$$CaCO_3 \text{ heated } = CaO + CO_2$$

The carbon dioxide is pumped to the towers to carbonate the brine, in the second principal process.

Of the quicklime produced, one portion is used in the second subordinate process (for recovery of ammonia).

Second subordinate process. In this operation, ammonium chloride, derived from the third principal process, is decomposed by milk of lime:

$$2NH_4Cl + CaO_2H_2 = 2NH_3 + CaCl_2 + 2H_2O$$

The ammonia gas liberated is used in the first principal process. The calcium chloride is to a considerable extent thrown away.

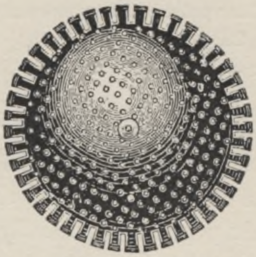

Fig. 16. Top view of perforated diaphragm for Solvay carbonating tower.

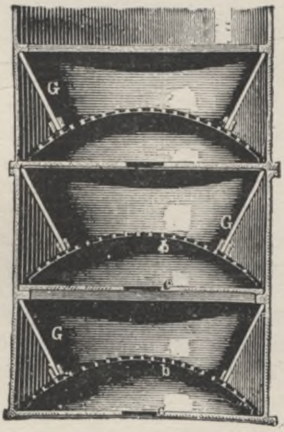

Fig. 17. Vertical section of portion of Solvay carbonating tower. The carbonic gas is distributed by means of the perforations in the diaphragms.

The Second Department. — The manufacture of caustic soda. In this department caustic soda, NaOH, is made from soda-ash by use of calcium hydroxide. (It has been described already at p. 37.)

In the ammonia-soda process, then, the following materials are demanded:

1. Common salt. The sodium of the salt goes into the finished product. The chlorine passes through two stages: First, it forms ammonium chloride, later it forms calcium chloride (the most of which is thrown away).

2. Limestone, calcium carbonate, $CaCO_3$. Of the carbon dioxide derived from this substance the larger part goes into the finished product, the soda-ash sold. A smaller part eventually combines with lime again in the causticising process (this portion is largely thrown away).

The calcium oxide serves its first purpose as an agent for the recovery of ammonia (in which case it is largely thrown away as calcium chloride). It serves its second purpose as a causticising agent (in which case it is largely thrown away as calcium carbonate).

3. Ammonia gas. This substance changes, in the towers, to ammonium chloride. Afterward the ammonium chloride is decomposed by milk of lime forming ammonia gas and calcium chloride. The ammonia gas is used over again; the calcium chloride is largely thrown away. There is always a small loss of ammonia, however; it has to be made up by new purchases.

4. Coal and coke. These are used as fuel (the coke in the lime-kilns).

The principal commercial products of the ammonia-soda works are:

1 — Soda-ash, Na_2CO_3,

2 — Sodium hydroxide, NaOH.

Fourth — The Electrolytic Process.

Of the sodium chloride used in the Leblanc process one-half of the chlorine, and of the sodium chloride used in the ammonia-soda process practically all the chlorine, is thrown away. Moreover, with it, in these cases, other substances, as lime and ammonia gas, are thrown away or lost incidentally.

For a long time chemists have been trying to avoid such losses. An important suggestion has been to decompose salt electrically. It has been assumed that by such an operation both sodium and chlorine may be utilized completely.

It is chemically possible to electrolyze *dry* sodium chloride so as to obtain free chlorine gas and metallic sodium; but it is difficult to perform the operation at a low cost. This particular process must be conducted out of presence of water; then the electrolyte must be in a state of fusion. But to secure this condition, high temperature is necessary; this involves considerable expense. Again, the sodium obtained, being of a low specific gravity, will come to the surface of the "melt"; this may occasion loss by volatization or by union with oxygen of the air, or by reunion with the chlorine from which it has just been liberated.

When a *water solution* of sodium chloride is electrolyzed, chlorine gas is liberated and sodium hydroxide is formed. But certain difficulties arise:

The chlorine tends to combine with the sodium hydroxide, producing sodium hypochlorite and chlorate. (Attempts have been made to overcome this difficulty by interposing porous diaphragms between the electrodes. These indeed keep the products of electrolysis apart, but they make a considerable increase in the electrical resistance of the system. Moreover, they are objectionable in the increased complexity of construction involved.)

In this case, as in most electrolytic work, the electrodes are liable to serious corrosion. The cathodes may be made of iron, but the anodes are generally made of some form of carbon.

Several ingenious systems contemplating the avoidance of as many as possible of the existent difficulties in the operation under discussion have been devised. Only one will be discussed here.

The Castner electrolytic process. — Two large works for the industrial conduct of this process on a large scale are at work (at the close of the year 1898); one in England and one at Niagara Falls in the United States. They are said to be highly successful.

The principal operation is conducted in a decomposing cell made of slabs of slate. This cell is about eight feet long, about three feet wide, and about one foot high. It is placed about three feet from the floor of the room, on a support which mechanically tilts it on its axis back and forth slightly but continuously. The cell is divided vertically by partitions into three compartments; as constructed these are all connected *at the bottom of the cell;* but *when in operation the connecting openings are stopped* by a layer of mercury resting on the bottom of the cell.

The *middle compartment* receives a slow but steady current of pure water. In the bottom of this compartment (under the layer of mercury and in contact with it) is an iron cathode; as a result the whole layer of mercury becomes a cathode.

Both *side compartments* receive a slow but steady current of brine; in each of the compartments is a large carbon anode.

The working is somewhat as follows:

The electric current decomposes the salt in the lower *side-compartment;* chlorine gas is liberated (it is pumped through a tube to the lime chamber, where it produces bleaching powder); the sodium is at first deposited as metal in the mercury cathode forming sodium amalgam. But the tipping motion of the whole cell leads the amalgam to run toward the other *side-compartment;* as it passes the *middle compartment* the sodium amalgam is *electrically* decomposed, thus forming sodium hydroxide, which dissolves, and clean mercury, which remains.

(The solution of sodium hydroxide flows away to a receiver and is evaporated. It produces a practically pure caustic soda, NaOH.)

The cell tilting back and forth repeats the operations described.

In this process the electric efficiency is high (as no diaphragms are used, and as the stratum of brine between the electrodes is thin, and for other reasons); the products of electrolysis do not recombine; the whole apparatus is of industrial form (of large units, and practically automatic). The iron electrode is permanent; the carbon electrodes (made by special process) are said to be durable.

Some persons predict that the electrolytic methods of decomposing common salt will soon entirely displace the methods now in vogue. Perhaps this may be true of the Leblanc process; but it does not seem probable of the ammonia-soda process. It appears that, at present, the gross weight of bleaching powder demanded by the world is far less than that of the sodium compounds (including soda-ash, caustic soda, and bicarbonate of soda). Now if a large electrolytic plant, operating to-day, were able to make all the bleaching powder demanded by the world, its corresponding output of sodium compounds would be far too small. The balance of sodium compounds, it appears likely, can be made in the cheaper manner by the ammonia-soda process (especially as electrolysis does not make *soda-ash* at as low a cost, relatively, as it produces *caustic soda*).

Second Appendix to Sodium. — Glass.

If silicon dioxide, SiO_2 (often called silica), and sodium carbonate, Na_2CO_3 (soda-ash), are fused together, carbon dioxide escapes as a gas, and solid sodium silicate — a kind of glass — is produced. This glass may be viewed as a compound of an acid oxide, SiO_2, with a basic oxide, Na_2O — that is a salt, sodium silicate.

Commercial glass is a much more complex compound than that referred to. But while, in it, there is little occasion for change in the matters of its acid oxide (although, in certain cases, boric oxide or phosphoric oxide are added) there are considerable opportunities for replacing or adding one or more basic oxides (thus potassium oxide, calcium oxide, lead oxide and some others are frequently added, singly or in groups). The additions of such oxides give rise to important and often valuable modifications in the properties of the glass produced.

Glass may be defined, in a general way, as a mass of interdiffused mixed silicates, in which silicon dioxide is present to the extent of about two-thirds of the finished product.

In stating the "batch" of materials melted together to produce glass it is customary and convenient to base the quantities on 100 parts of silica used. Thus the following simple "batch" produces a melt suitable for making plate glass:

SiO_2	100.	parts
Na_2CO_3	33.30	"
CaO	14.30	"
MnO_2	.16	"

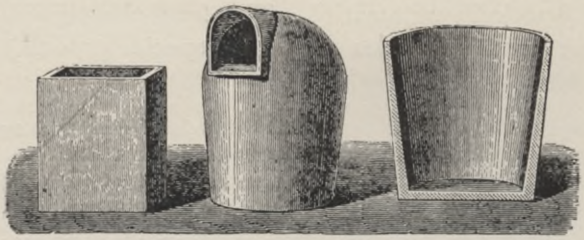

Fig. 18. Various crucibles or "pots" for melting a mixture of soda-ash, etc., sand, in producing glass.

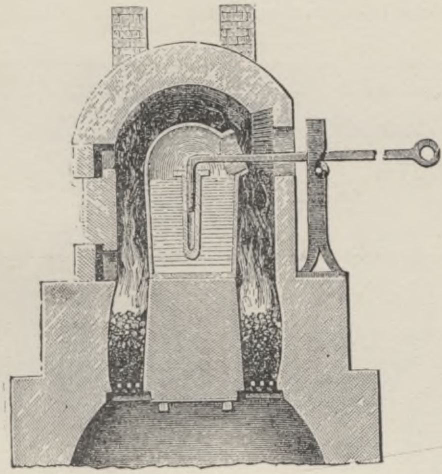

Fig. 19. Section of furnace and "covered" pot for melting glass that is subjected to injury from the furnace gases. (The batch may be stirred by a special appliance — an iron poker coated with a clay "sleeve.")

As a result of fusion, carbon dioxide is expelled and a sodium calcium silicate is produced. The weight of finished glass is about 87 per cent. of that of the batch. (In other cases the product may be relatively greater or less than in this.)

— In the older types of glass furnaces, the batch is melted in a large crucible or "pot" made of carefully selected and thoroughly manipulated clay. Open pots are employed in many cases, but if gases from the furnace are capable of injuring the color of the glass, a pot, hooded at the top and having an opening at the side, is employed.

In large glass works, producing ordinary articles, *tank furnaces* are now considerably used. The tank is made of blocks of selected and manipulated clay. At the rear end, the materials constituting the batch are introduced. Along the sides of the tank, blasts of gas are introduced. The gas is either natural gas, or that called *producer-gas* (made by passing steam through hot coal or coke, so as to yield a mixture consisting principally of hydrogen and carbon monoxide). The gas, burning in great volume over the surface of the batch, melts it. Soon the tank becomes a lake of molten glass. A rake-like clay contrivance, on the surface of the molten batch, skims it. At the forward end of the tank are

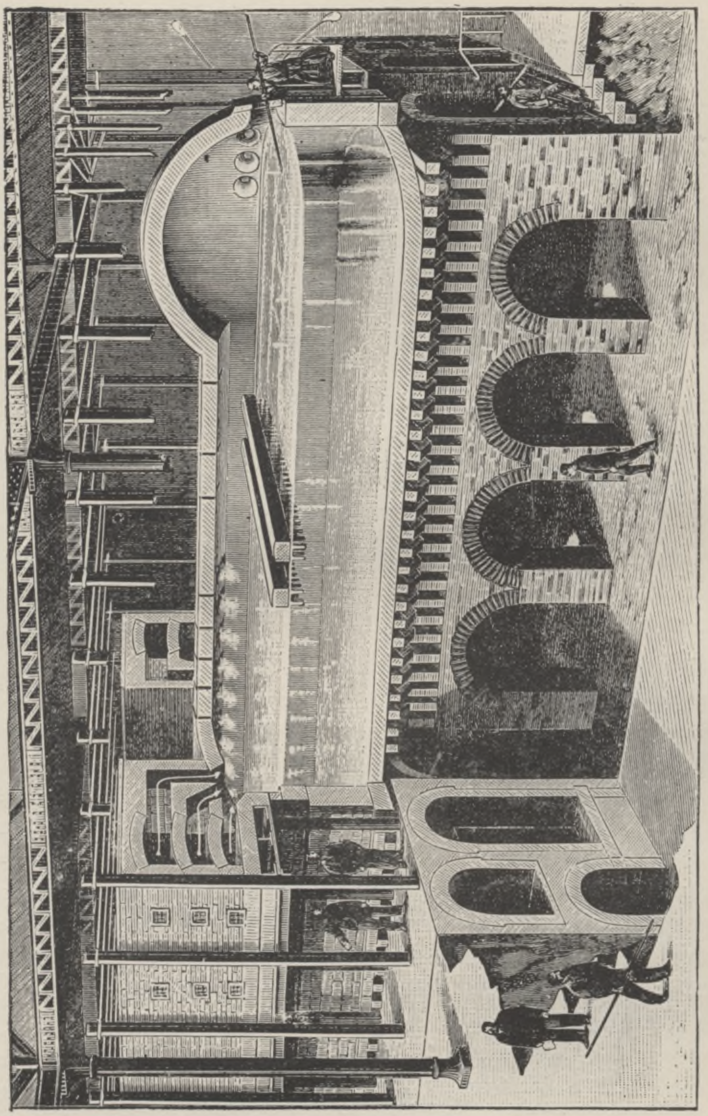

Fig. 20. In modern glass furnaces the batch is often melted in a large covered tank made of blocks of fire-brick. The raw materials are introduced at the rear (on the left). The batch is heated by *gaseous* fuel. The working openings are at the right.

openings through which the glass blowers can obtain their supplies of melted glass. This tank system can be used for a long time continuously.

— In making window-glass, a long cylindrical bulb is blown; after it has cooled a little, the ends are cut off, one side is cut open, and the tube is then spread out into a sheet which may be subsequently cut into pieces of appropriate size.

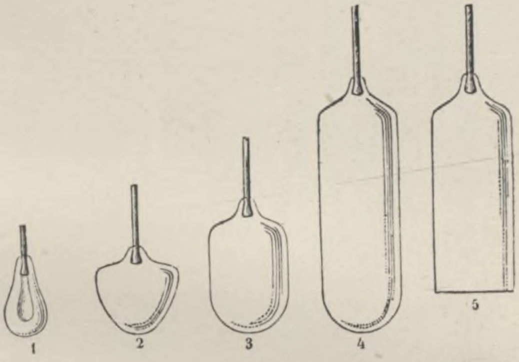

Fig. 22. In melting window-glass a portion of melted glass is gradually enlarged to a bulb having an elliptical section (4). Later, one end is opened (as in 5). Subsequently the other end is similarly opened so as to form a large tube.

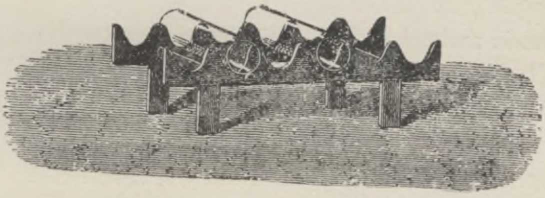

Fig. 23. Window-glass tubes awaiting the flattening process.

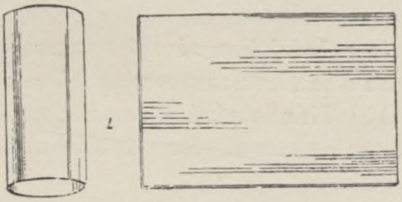

Fig. 24. A window-glass tube is cut lengthwise, then spread out flat.

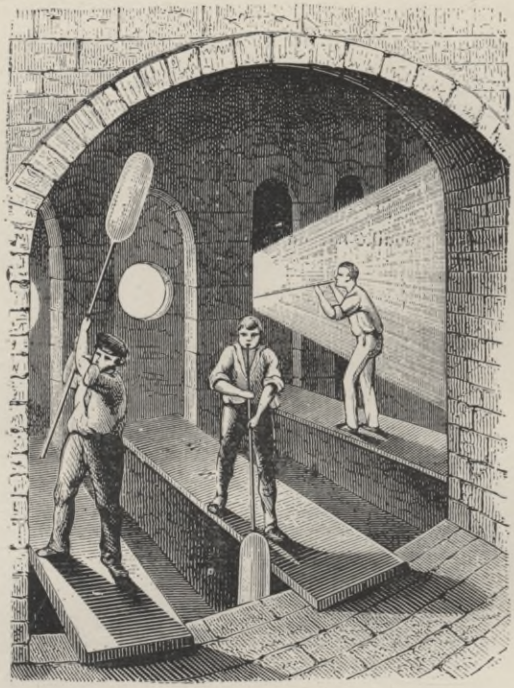

Fig. 21. Window-glass is first blown into long bulbs of elliptical section.

Plate glass is melted in pots and then poured upon a large level surface. The sheet of glass thus obtained is afterward ground so as to give it plane surfaces. Subsequently, the surfaces are polished.

The recipe given earlier in this Appendix is a very simple one: a multitude of other substances may be employed either singly or together. The intention may be to lower the cost, or to produce some specific quality (as high refractive power, which gives brilliancy) or to produce a distinct color, or to do something else desirable.

The following is a brief list of substances employed in the batch together with a few comments upon them:

1. — Silica, SiO_2. This is used in form of sand or otherwise. For glass of high quality the mineral should be as free as possible from compounds of iron.

In some cases the sand is heated to redness in a furnace before use. As a result, the material is rendered finer and, subsequently, it enters more readily into combination with the other constituents of the batch. One result is a saving of time and fuel.

Sometimes quartz and flint are heated to redness and then thrown into water. Washing with hydrochloric acid helps to rid the sand of iron, but ordinarily the process is too expensive.

In a few cases natural silicious rock material may be fused alone, so as to produce an inferior glass. Minerals like feldspar, which are more difficult of fusion, are sometimes employed in connection with other materials.

2. — Soda-ash, Na_2CO_3. The ash now used is of a very high degree of purity. The ash formerly used, whether made by burning marine plants or else by the early forms of the Leblanc process, was very impure.

Attempts have been made to use common salt as a substitute for soda-ash. In the pot the salt is readily decomposed by the sand. Two difficulties arise, however; the heat of the furnace is so great that common salt is largely volatilized, — again, this salt attacks the walls of the furnace.

3 — Salt-cake, Na_2SO_4. This supplies sodium oxide in a cheap form. Sometimes it is partly decomposed to sulphite by heating with powdered anthracite coal before use; in either case it is used in batch together with just enough carbon to change it to sulphite.

4. — Potassium carbonate, K_2CO_3.

5. — Calcium oxide, CaO, or calcium carbonate, $CaCO_3$. These substances are used for the purpose of supplying calcium oxide, which improves the quality of the glass.

Quick-lime that is air slaked is preferred, because it is very finely divided and it evolves less carbon dioxide than limestone does.

The calcium compounds must be regulated in quantity by the sand present. An excess of calcium compounds abstracts silica from the pots and injures them.

6. — Lead oxide, or litharge, PbO, and red-lead, Pb_3O_4. These oxides form easily fusible silicates — they make the batch melt well. They add to the density of the glass thus making it more brilliant. Lead glass is called "flint glass," it is the glass used in common table ware. Red-lead is highly oxidizing, which is valuable — it helps to decolorize a batch containing ferrous oxide. (See 7)

7. — Iron compounds. These are often present as impurities in the sand used. The ferrous oxide gives a green color; the ferric oxide imparts but little color. (See 8.)

8. — Manganese dioxide, MnO_2. This is sometimes called the "glass-maker's soap." It oxidizes the iron compounds to colorless ones — itself is simultaneously reduced to a colorless compound. A small excess of manganese dioxide gives a pink color. Two or three per cent. gives an amethyst color (but if this is desired, four or five per cent. of saltpetre should be added to prevent reducing action).

9. — Potassium nitrate, KNO_3. This substance is occasionally employed in small quantities as an oxidizing agent. It may destroy particles of carbon which sometimes stain the glass badly. It may act as described above (No. 8) in oxidizing iron compounds.

10. — White arsenic, arsenious oxide, As_2O_3. This substance is frequently used as an oxidizing agent. But it seems to exert beneficial offices less well understood.

11. — Broken glass or "cullet." Cullet is almost invariably used. Waste glass is carefully cleaned and ground, and then introduced in proper proportions in the batch. It has a very favorable influence. It seems to assist materially the union of the various raw materials of the batch.

Glass is colored by the addition of certain substances, chiefly *metallic oxides*, to the batch (but carbon gives a black color when present in large quantity, and an amber color when present in small quantity). Cobalt oxide is used to produce blue glass; manganese dioxide for purple glass; uranium oxide gives a peculiar yellowish green color called canary. Certain compounds of gold give a ruby color. It is not known in what condition the gold exists in the finished glass. Perhaps it is in a very finely divided metallic form.

POTASSIUM; K; 39,11.

Introduction — Distribution, preparation, properties of potassium — Compounds of potassium, especially bromide, iodide, oxide, chlorate, nitrate.

First appendix — The Stassfurt deposits of potassium compounds.
Second appendix — Potassium compounds as agricultural fertilizers.
Third appendix — Explosives.

Data for Reference.

Density of solid potassium, .875 (water being the standard = 1).
Fusing point of solid potassium, 62.5° C.
Boiling point of liquid potassium, 719° — 731° C.
Potassium was discovered by Sir Humphry Davy in 1807.
The word potassium is a manufactured word of Latin form. It is derived from the English word potash.

Introduction.

1 — Potassium compounds are important from two different classes of considerations. On the one hand they are of great service in agriculture because of the *potassium* contained in them. On the other hand many potassium compounds are of wide use in the arts because of *the other constituents* — the potassium of such compounds being largely, though not entirely, incidental. (Potassium nitrate is an example.)

2 — Potassium compounds are generally higher priced than the corresponding sodium compounds. The chief reason is found in the fact that, while the aggregate amount of potassium in the earth appears to be about the same as that of sodium, yet the amount of *easily accessible potassium compounds* is far less than that of easily accessible sodium compounds (especially common salt).

3 — Potassium was discovered by Sir Humphry Davy in the year 1807. Upon submitting a fragment of potassium hydroxide to the action of a powerful galvanic battery, he obtained small globules of a substance having a high metallic luster — as he

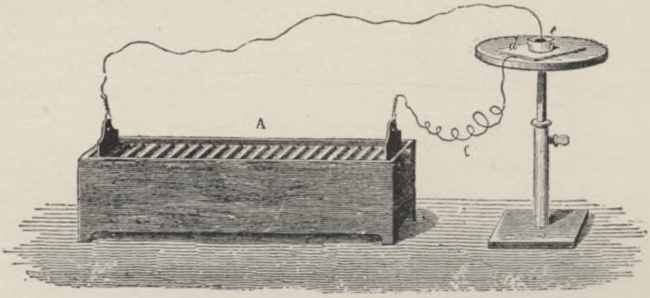

Fig. 25. Sketch of apparatus similar to that used by Davy in the discovery of potassium. At A is the galvanic battery; at *e* is the platinum dish containing potassium hydroxide to be electrolyzed.

describes it — resembling quicksilver. This was at once recognized as a most important discovery.

— It showed the importance of the electric current as a means of chemical decomposition.

— It suggested the possibility of the discovery of yet other elements by the use of this appliance. Indeed the discovery of the important metals, sodium, barium, strontium, calcium, quickly followed Davy's notable experiment.

— It led to the immediate suggestion that many substances previously undecomposable and considered as elements might be found, by further examination, to be compounds.

It may be added that while batteries were somewhat used in Davy's time, no practical application was made of this kind of electrolysis. But at the present day the electric current is largely employed in the practical separation of metals from their compounds.

Distribution of Potassium.

Potassium is not found *free* on this earth, but it exists very widely distributed in combination with other substances.

First — Compounds of potassium exist in some well defined minerals: for example the variety of feldspar called orthoclase, potassium aluminium silicate, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, contains 14 per cent. of potassium.

Feldspar is a constituent of granite, but while granitic rocks are very abundant, potassium is not produced directly from this source.

Second — The so-called Stassfurt deposits consist of an enormous mass of soluble salts containing among others, the minerals:

Sylvite, KCl;

Kainite, a hydrous potassium magnesium sulphate, with potassium chloride, $K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$.

Carnallite, a hydrous potassium magnesium chloride, $KCl, MgCl_2{\cdot}6H_2O$.

Stassfurt is a small town about twentyfive miles southwest of Magdeburg, Prussia.

Vast quantities of crude potassium chloride obtained from the Stassfurt mines are now used in commerce. The production appears also to be on the increase. Not far from half that produced is consumed in the manufacture of potassium nitrate — for gunpowder and other uses. About one-quarter is converted into carbonate — chiefly by a process analogous to the Leblanc process. About one-fifth is employed in agriculture, in commercial fertilizers. — (*Am. Ch. J.*, February, 1891.)

Third — Compounds of potassium exist in minute quantities in soils. Living plants have the power of selecting potassium salts from the soil, transferring such salts to their own structures.

When such plants are burned, potassium salts (mainly potassium carbonate) are found in the ashes. Wood ashes form an important article of commerce on account of the potassium salts they contain.

The ashes are treated with water. The liquid is filtered. The clear filtrate is boiled down until a solid mass is obtained. This mass consists mainly of potassium carbonate and potassium hydroxide. It contains many impurities. But it is suitable for certain common purposes for which a potassic alkali is required. Further purification of it may be practiced if necessary. Again, other salts may be prepared from it.

Fourth — It exists in small quantities in waters of certain mineral springs and of the Dead Sea and of the ocean.

Fifth — Sheep's wool contains a large quantity of greasy material, mingled with which are salts of potassium. The aggregate amount of potassium salts derived from the scouring of the vast amount of wool consumed in the world, is very considerable.

The greasy material is sometimes collected and heated in retorts. The organic matters generate certain gases which are used for illumination. The mineral matter left in the retort is rich in certain potassium compounds, and is used for the production of others.

Sixth — The "vinasses" of beet sugar works (a liquor left after the exhausted beet "chips" have been fermented) contains potassium compounds. At present it is not an important source.

Preparation of Potassium.

Potassium is usually prepared by heating a mixture of potassium carbonate and charcoal.

The process is carried on in a peculiar iron retort devised for the purpose. The proper mixture is introduced into the body of the retort, the neck of the retort being connected with a suitable receiver so adjusted as to avoid access of air. The retort and its contents are raised to a white heat, whereupon the potassium salt is decomposed.

The chemical change is represented by the following equation:

$$K_2CO_3 + 2C = K_2 + 3CO$$

The liberated potassium changes into vapor and passes over into the receiver, where it cools and condenses into portions of metal.

Properties of Potassium — Physical Properties.

Potassium is a silvery-white metal. It is the lightest metal known except lithium. It is soft and easily cut with a penknife. It melts and volatilizes very readily under the influence of moderate heat.

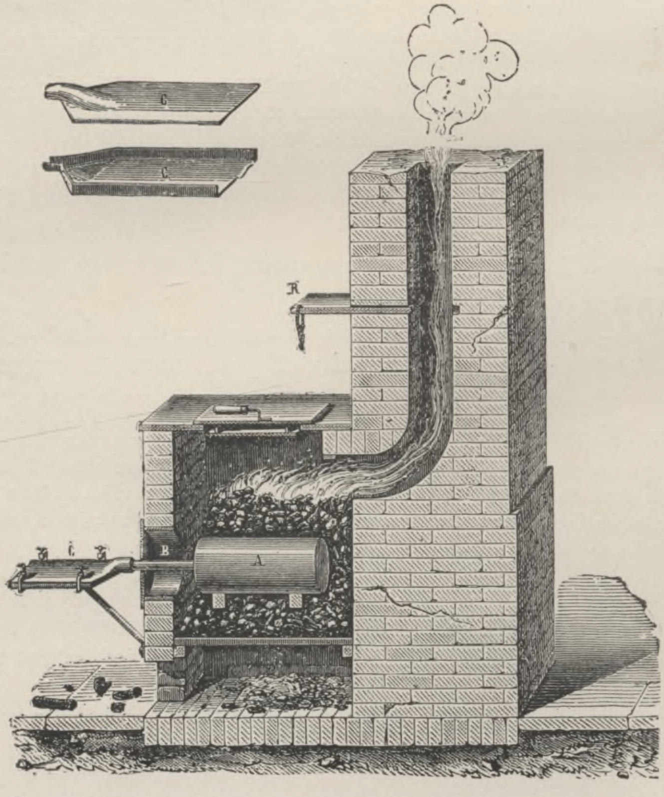

Fig. 26. Furnace used for the production of metallic potassium. A mixture of potassium carbonate and carbon heated in the retort yields potassium which vaporizes (but condenses in the receiver).

Properties of Potassium — Chemical Properties.

It has very strong electro-positive qualities. Upon exposure to the air it quickly oxidizes, forming potassium oxide, K_2O.

This substance at once absorbs carbon dioxide and water from the atmosphere. With the one it forms potassium carbonate, K_2CO_3; with the other it forms potassium hydroxide, KOH. Both of these substances absorb more moisture from the atmosphere, so that a piece of potassium exposed to the air becomes covered first with a whitish coat and later assumes a moistened appearance. Sometimes the potassium takes fire under these influences.

The affinities of potassium for oxygen and other electro-negative substances are very strong. On this account it easily draws them from other metals with which they are in combination. Such metals are then brought to a metallic condition. This kind of action is commonly called a *reducing* action.

A Few Compounds of Potassium (with elements already discussed).

With hydrogen;	Potassium hydrogenide, K_4H_2	
With fluorine;	—— fluoride, KF;	Potassium hydrogen fluoride, KHF_2
With chlorine;	—— chloride, KCl	
With bromine;	—— bromide, KBr	
With iodine;	—— iodide, KI	
	—— tri-iodide, KI_3	
With oxygen;	Potassium monoxide, K_2O;	Potassium hydroxide, KOH
	—— peroxide, K_2O_4;	—— hypochlorite, KClO
		—— chlorate, $KClO_3$
		—— perchlorate, $KClO_4$
		—— bromate, $KBrO_3$
		—— iodate, KIO_3
		—— periodate, KIO_4
With sulphur;	Potassium monosulphide, K_2S;	Potassium hydrosulphide, KSH
	—— disulphide, K_2S_2	
	—— trisulphide, K_2S_3	
	—— tetrasulphide, K_2S_4	
	—— pentasulphide, K_2S_5	
		Potassium sulphite, K_2SO_3
		—— hydrogen sulphite, $HKSO_3$
		—— disulphite, $K_2S_2O_5$
		—— sulphate, K_2SO_4
		—— hydrogen sulphate, $HKSO_4$

With tellurium;	Potassium telluride, K_2Te?	
With boron;		Potassium metaborate, KBO_2
With nitrogen;	Potassium nitride (triamide), NK_3 Potassamide, NH_2K	Potassium nitrite, KNO_2 ——— nitrate, KNO_3
With phosphorus;	Potassium phosphide (exists);	Potassium hypophosphite, KPH_2O_2 ——— phosphite, K_3PO_3 ——— orthophosphate, K_3PO_4 ——— pyrophosphate), $K_4P_2O_7$ ——— monometaphosphate, KPO_3
With arsenic;		Potassium arsenite, K_3AsO_3 ——— arsenate, K_3AsO_4
With carbon;	Potassium cyanide, $K(CN)$;	Potassium carbonate, K_2CO_3 ——— hydrogen carbonate, $HKCO_3$ Potassium cyanate, $KO(CN)$ ——— sulpho cyanate, $KS(CN)$
With silicon;	Potassium silico-fluoride, K_2SiF_6;	Potassium metasilicate, K_2SiO_3 ——— tetrasilicate, $K_2Si_4O_9$

Potassium chloride, KCl, potassium bromide, KBr, and potassium iodide, KI, are considerably used in the arts.

Potassium monoxide, K_2O. — This substance by uniting with water forms potassium hydroxide, called also potassic hydrate, and caustic potash, KOH.

Caustic potash is used as an alkali for a variety of purposes in chemistry. It is usually sold in the form of white sticks. In this form it is sometimes employed as a cauterizing agent in surgical operations.

Potassium chlorate, $KClO_3$. — This substance is a white salt largely sold in commerce in the form of glassy crystals.

It is employed in the manufacture of oxygen gas. It is also used in the tips of certain kinds of parlor matches. When the matches are rubbed, the oxygen liberated from the chlorate helps in the combustion. It is used for the same purposes in fireworks. It is largely used in calico printing, particularly in the production of the color known as aniline black. Potassium chlorate is employed as a gargle in certain throat diseases.

Potassium nitrate, also called saltpetre, and nitre, KNO_3. — Potassium nitrate is found in certain parts of India, as crusts on the earth, and it is carefully scraped from the soil for the purpose of purification into nitre.

Fertile soils contain calcium nitrate. It is produced by a special bacterium which has the power of changing nitrogenous organic matters into nitrates. Calcium nitrate by reaction with potassium chloride may form potassium nitrate.

In the great wars incident to the French Revolution, nitre was artificially manufactured from heaps of decaying animal matter by a process similar to that already described. The demand for gunpowder was very great and the blockade of French ports prevented the importation of nitre from India.

Potassium nitrate is now largely manufactured by the double decomposition of two salts found in certain large deposits. These are Chile saltpetre, sodium nitrate, $NaNO_3$, and Stassfurt potassium salts, potassium chloride, KCl. By proper management the change represented by the following equation may be accomplished:

$$NaNO_3 \quad + \quad KCl \quad = \quad KNO_3 \quad + \quad NaCl$$

The sodium chloride of this operation may be crystallized out, leaving the saltpetre in solution. By subsequent treatment the saltpetre may be crystallized and separated from this solution.

Potassium nitrate is of great commercial importance. Its chief use is in gunpowder and in pyrotechnics. A considerable quantity is also employed for the preservation of salted meats. Vast quantities of it are used in blasting powder as well as in war powder. In all these cases its use depends upon the presence of nitrogen rather than on that of potassium.

Uses of Potassium Compounds.

Potassium compounds are of great importance in the arts. In some cases this importance is referable directly to the potassium itself. In some cases it is indirect, that is, the potassium is a convenient vehicle to which the directly useful substance may be attached.

Direct use of potassium compounds. — All potassium compounds are useful in agriculture, because the potassium itself is a necessary food for plants. The element or elements incidentally combined with the potassium may, however, be favorable or unfavorable to the growth of plants, or, again, they may be suitable by reason of cheapness, or unsuitable by reason of high price.

Indirect use of potassium compounds. — 1. Potassium compounds are largely used in chemical operations. Oftenest, the potassium is merely incidental, — the compound employed is useful because of the other elemenet or elements present. Thus potassium dichromate has long been largely used in the arts, chiefly on account of its chromium compound. It has long been recognized that sodium dichromate would be cheaper so far as the metals sodium and potassium are compared, but potassium dichromate crystallizes in a comparatively pure form much easier than sodium bichromate. This fact has dictated an enormous use of potassium dichromate. However, in recent years, chemists have devised methods of producing, at reasonable prices, sodium dichromate for use in the arts.

2. Potassium nitrate is largely used in gunpowder and blasting-powder. The constituents of primary importance in the salts mentioned are nitrogen and oxygen. While sodium nitrate would serve, it is not as good as potassium nitrate, because sodium nitrate in gunpowder absorbs from the atmosphere much more moisture than potassium nitrate does. Thus the usefulness of potassium, in this case, is a real one, although subordinate to that of the nitrogen-oxygen group.

First Appendix.—The Stassfurt Deposits of Potassium Compounds.

Common salt has been made from the brine of the Stassfurt salt wells since the year 1227. But in 1815 unfavorable business conditions suspended this work. From 1839 to 1852 the territory was carefully explored by means of new wells drilled. It was found that the deposit of solid salt is about 2,500 feet thick.

It has long been known that the deposit, like others of a generally similar character, contains certain impurities. But it is only since 1860 that the importance of those substances, other than salt, present in the deposits, has been appreciated. Since that date large works have been established at Stassfurt, and at the neighboring town of Leopoldshall, especially for the working of the potassium compounds. Moreover, the deposits have been most carefully studied from the chemical and geological points of view.

The strata have been classified in four groups of layers called "regions":

1st. The Anhydrite region.—It is about 2,000 feet thick. The salt is penetrated by thin layers of the mineral anhydrite, calcium sulphate, $CaSO_4$. (Salt, 90–95 per cent.; anhydrite, 4–9 per cent.)

2d. The Polyhalite region.—It is about 207 feet thick. The salt is mixed with a variety of minerals. The principal one is polyhalite, a calcium-magnesium-potassium sulphate, $2CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$. (Salt, about 91 per cent.; polyhalite, about 6–7 per cent.)

3d. The Kieserite region.—It is about 187 feet thick. The characteristic substance is kieserite, a monohydrated magnesium sulphate, $MgSO_4 \cdot H_2O$. (Salt, about 65 per cent.; kieserite, about 17 per cent.)

4th. The Carnallite region.—It is about 140 feet thick. The chief component of this important region is not salt but carnallite, a potassium-magnesium chloride, $KCl \cdot MgCl_2 \cdot 6H_2O$. (Salt, about 25 per cent.; carnallite, about 55 per cent.; other magnesium salts make up the balance.)

The richness of this particular region in potassium compounds makes it the portion of chief commercial importance.

The method of working the Stassfurt deposits varies according to the special portion of the deposit in hand. The process for carnallite briefly stated is as follows: The crude carnallite as brought to the surface is acted upon by water (or better by mother-liquor of previous operations). A solution as rich as possible in potassium chloride is secured. Later this solution is concentrated by evaporation. But the dissolving and the evaporation are conducted in subjection to the most critical chemical principles so as to accomplish the separation of the potassium salt as economically as possible.

The principal commercial products from the Stassfurt deposits are:
— Potassium chloride (in several grades),
— Epsom salt, $MgSO_4 \cdot 7H_2O$ (made from kieserite),
— Glaubers salt, $Na_2SO_4 \cdot 10H_2O$,
— Magnesium chloride, $MgCl_2 \cdot 6H_2O$,
— Bromine,
— Boric acid,
— Agricultural fertilizers.

The latter, called manure salts, are made from by-products dried and ground. They are adjusted so as to contain the proper percentage of potassium, moreover, this substance is supplied in the form of *sulphate* rather than *chloride* (since potassium *chloride* is a less favorable plant food); again magnesium chloride is removed as far as possible (since it is noxious to growing plants).

The Stassfurt deposits were formed by intermittent evaporation of ocean water. They probably required a period of about 8,000 years for their production. The territory in which they exist was probably a lake, separated from the ocean only by a bar in which a narrow opening allowed occasional ingress of sea water and occasional egress of mother-liquor. As the water of the lake evaporated during the course of centuries salt was deposited and with it other compounds according to the conditions prevailing. Sometimes disturbances of strata threw mother-liquor back into the ocean — sometimes a new supply of brine came into the lake. The details of these intermittent changes have been so computed as to account for the various formations and also for the fact that the deposits are of a slightly different composition from that which would have been afforded by a direct and continuous evaporation of ocean water.

Second Appendix. — Potassium Compounds in Agriculture.

The growing plant demands as food a considerable number of elementary substances. It obtains some of them from the atmosphere, some of them from the soil. While certain of these elementary substances are at hand in great abundance, there are three that exist in soils in relatively small quantity. The three elements in question are nitrogen, phosphorus, and potassium;

nitrogen and phosphorus are discussed with propriety among the non-metals; potassium may be properly referred to here.

It is a matter of certain experimental knowledge that, in all ordinary cases, addition of solutions of potassium salts to soils of plants growing in pots promptly stimulates growth. Hence, in the intelligent compounding of agricultural fertilizers, potassium compounds are always provided.

In nature, soil may gain potassium compounds from the disintegration of *granite rocks;* but the process is slow.

Potassium compounds may be artificially supplied by fertilizing with *wood-ashes,* and such is a common practice: wood-ashes obtained from sparsely populated territory, like that of Russia and of Canada, are furnished commercially for agricultural use.

Potassium nitrate obtained in India is an exceedingly valuable fertilizer on account of its content of nitrogen in addition to that of potassium. But nitre makes no figure in commercial fertilizers; practically, all that is produced is consumed in the manufacture of explosives.

The chief source of supply of potassium compounds for agriculture is found in the minerals of the *Stassfurt deposits,* and these deposits have thus become of great value to mankind.

Third Appendix. — Potassium Compounds in Explosives.

The principal explosives in use, whether for blasting rock material on the surface or in mines, or for fireworks, or for war purposes, may be discussed in three groups, namely: gunpowder, organic nitrates, commonly called nitro-compounds, and the fulminates.

In all these cases the explosive effect is referable to *comparatively sudden liberation of a large amount of gas,* by reason of some kind of breaking up of the molecules of the explosive substance. The explosives generally demand the presence of some compound or compounds *containing at once nitrogen and oxygen,* and the reaction which gives off expanding gas generally depends on the instability of the nitrogen-oxygen compound. Ultimately, the proper nitrogen-oxygen material is derived either from natural deposits of potassium nitrate or of sodium nitrate. But these compounds are not abundant in the earth; they are formed only under the influence of microscopic bacteria through long periods of time; they are in enormous commercial demand in agriculture as well as for explosives. Thus the natural stores of them assume a great importance; they should be judiciously economized.

Gunpowder. — The word gunpowder has long been employed, but the substance is never a *powder.* It is carefully formed into *grains* of various shapes and sizes. Old-fashioned gunpowder is essentially a mixture of potassium nitrate, charcoal, and sulphur. Certain kinds of charcoal afford black powder, others afford brown or cocoa powder.

Although the burning of powder appears to be instantaneous, it is not so. It proceeds step by step. By proper management, the burning may be made to proceed at a definite desired rate.

The approximate composition of gunpowder is as follows:

Potassium nitrate (saltpetre)	75	per cent.
Carbon	$12\frac{1}{2}$	"
Sulphur	$12\frac{1}{2}$	"
	100.00	"

The so-called nitro-compounds. — A typical compound of this group is that called nitro-glycerin. This substance is more properly a nitrate, propenyl nitrate, $C_3H_5(NO_3)_3$. Gun-cotton, a cellulose nitrate, belongs to this group. These substances are appropriately discussed under organic chemistry rather than here.*

Fulminates. — The fulminates are metallic salts of a peculiar nitrogen acid called fulminic acid. Silver fulminate and mercury fulminate are much used; The former in toy torpedoes, the latter in the exploders of many kinds of ammunition and war material.

Smokeless powder. — In modern armies the tendency is toward the use of quick-firing magazine rifles of small bore (about .25 inch). In order to avoid the liability to foul, associated with ordinary powder, and for other reasons, what is called smokeless powder is now used.

Smokeless powder consists chiefly of cellulose nitrates (gun-cotton), but it usually contains some nitro-glycerin. Occasionally it contains small quantities of metallic salts. In one of the stages of its preparation it is a soft paste; subsequently the paste is made into pellets, or rods, or sheets, or other geometrical forms.

Burning of gunpowder. — When gunpowder is burned, a very complicated series of chemical changes take place. The following equation serves as a general statement:

$$2KNO_3 + 3C + S = 3CO_2 + N_2 + K_2S$$

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* See the author's *Carbon Compounds.*

The carbon dioxide and the nitrogen are gases. Moreover by the heat of the combustion they are in a very much expanded condition. When explosion takes place the great volume of liberated gas propels the bullet — or in blasting rends the rock.

The potassium sulphide, K_2S, in the form of fine powder or dust makes a considerable part of the smoke that is noticed. It also remains to some extent in the barrel of the piece and fouls it.

The potassium nitrate oxidizes the carbon, producing at once the gas generated, and the heat which expands this gas.

The potassium nitrate. — While almost any nitrate may be used directly or indirectly for most explosives, the potassium nitrate is the one best fitted for use in ordinary gunpowder — it is preferable to sodium nitrate because the latter absorbs moisture (as potassium nitrate does not), and moisture seriously disturbs the *intimate admixture of substances,* necessary to good gunpowder.

As has been stated the stock of potassium nitrate derived from the soil of India is practically all employed for the manufacture of gunpowder; yet it does not satisfy the demand. The additional supply of potassium nitrate is artificially prepared by the interaction of Chile saltpetre (sodium nitrate) and potassium chloride from the Stassfurt deposits.

In certain cases a nation at war finds itself unable to import either potassium nitrate or sodium nitrate, that is, to secure either of these essential substances from the greatest natural available stocks of them. It must then have recourse to those stocks sparsely distributed in its own soil. In almost all soils there exist nitrifying bacteria; these act on decaying nitrogenous matter changing it, in minute portions, to nitrates, — chiefly calcium nitrate. If such soil is stirred with water and then the liquid is filtered from the earthy material, the watery filtrate contains the calcium nitrate. Subsequent addition of a potassium compound, e. g., potassium carbonate, gives rise to the formation of potassium nitrate, which latter is the one desired for gunpowder.

During the Civil War in the United States, the Confederates were obliged to resort to processes of this general character.

Twice in the history of France, first, during the French Revolution in 1793, and second, during the siege of Paris in 1870, the demand for potassium nitrate for use in the manufacture of gunpowder has become so imperative that the substance has been manufactured from nitrate in the soil of a region not largely productive.

December 4, 1793 (an II, 14 Frimaire), the Committee of Public Safety invited all citizens to lixiviate nitrated earths under or about their houses. The republic was divided into eight arrondissements, each of which was supplied with an inspector having ample chemical knowledge. Further, an official was appointed for each subordinate department, to instruct a larger number of agents, furnished for each small district. The main committee in charge was divided into three sub-committees: a committee on saltpetre, Fourcroy, Plouvinet, and Defourny; one on gunpowder, Guyton, Carny, Berthollet; one on cannon, Hassenfratz, Monge, Perrier. These committees gave lectures in the forenoon to a certain number of pupils in the city of Paris. In the afternoon, the pupils visited the various saltpetre works then actively at work. Upon the completion of the course of lectures, all Paris united in a festival, at which the saltpetre produced by the pupils from the earth under the barracks was presented to the nation with French ceremonial. Later, the pupils were distributed to different districts to teach others how to carry on the processes.

In 1870 a similar committee was appointed. It was composed of Berthelot *as President*, Bréguet, D'Almeida, Fremy, Jamin, Ruggieri, Schutzenberger. Since the city of Paris was besieged, it was necessary for the inhabitants to manufacture gunpowder from materials obtained from their own soil. In an interesting report presented by Berthelot, reference was made to a report of 1786 and to others dating as far back as 1540.

The details of Berthelot's reports relate to three topics: *first*, the richness in nitrates of the natural available materials; *second*, the best method of collecting such materials; *third*, a method for a general securing of the useful material through the city of Paris.

The methods proposed to be practiced by all the inhabitants of the city were the following:

First, they were to scrape from cellars and sub-cellars, especially from those near stables, any efflorescences on the walls and the soil adjacent. They were to brush or gently scrape the walls of cellars (especially of old buildings), outside and inside. They were to save the solids thus secured.

Second, they were to save plaster from old buildings demolished.

Third, they were to excavate about four inches of the soil of cellars, stables, and stable yards, and to do the same for garden soils.

Fourth, they were to place wood-ashes saved from household fires, in three tubs side by side. Then to these ashes, they were to add the soil and other nitrated material collected as above described. Next, water was directed to be leached from one vessel into another. The liquid obtained by this filtration was to be boiled down or evaporated until it possessed a strength of from five degrees to six degrees by the areometer. Finally this liquid was to be delivered to agents who were to collect from house to house.

In order to carry out these operations, one month's time was assigned and eighty agents were appointed. The agents were to deliver the liquids at the twenty factories in operation in the city. In these factories the work was to be completed.[*]

The theory of these operations is evident: lixiviation of cultivated soil yields a water solution containing calcium nitrate; lixiviation of wood-ashes yields a water solution of potassium salts, principally carbonate; when these solutions are mixed and the mixture filtered, a liquid containing potassium nitrate (saltpetre) is secured; when this liquid is evaporated to dryness solid potassium nitrate is obtained.

AMMONIUM; NH_4; 18,072.

Ammonium is a compound radicle having the formula NH_4. It has not been prepared in a separate form. It exists only in combination with other elements or compounds. Many compounds of ammonium correspond closely with compounds of the alkali metals. Indeed, it acts in many ways distinctly like a metal. It is often spoken of as the hypothetical metal.

Its composition seems to relegate it with propriety to the portion of chemistry which treats of the non-metals.

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[*] Helene, M.— *La poudre a canon*, Paris, 1878.

CAESIUM; Cs; 132, 89.

Introduction — Distribution, preparation, and properties of caesium — Compounds of caesium.

Data for Reference.

Density of solid caesium, 1.88 (water being the standard = 1).

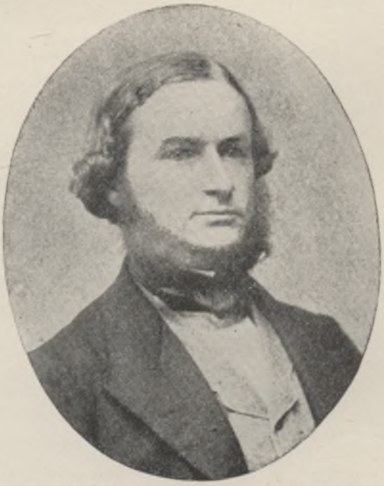
Fusing point of solid caesium, 26° — 27° C.

Caesium was discovered by Bunsen and Kirchhoff in 1860.

The word caesium is derived from the Latin word *caesius*, bluish gray (the reference is to two sky-blue lines in the spectrum afforded by caesium compounds).

Introduction.

In 1860 Professors Bunsen and Kirchhoff were at work with their new invention, the spectroscope. Upon applying this instrument in the examination of certain mineral residues obtained after evaporating immense quantities of Dürkheim mineral spring water they obtained certain unusual spectral lines. Upon following up the subject they discovered that these lines were caused by two previously undetected metals : caesium and rubidium.



Gustav Robert Kirchhoff, b. in Königsberg 1824; with Bunsen, inventor of the spectroscope.

As early as 1846 the German chemist, Plattner, found a certain discrepancy in the results of his analysis of a rare mineral called pollux. This difficulty was not explained until the spectroscope was invented. Then it was found that pollux is rich in caesium. In Plattner's analysis, the caesium (then unknown) had been counted as potassium.

Distribution of Caesium.

Caesium is never found free in nature. Its salts are very widely distributed, though in very small quantities. In caesium minerals the rare metal rubidium is often present as a companion. Caesium is found in certain mineral waters and in many minerals, especially in the lepidolite from Hebron, Maine. It also occurs in sea-water and sea-weed. It is found in the ashes of certain land plants, as oak, tobacco, tea, coffee.

Preparation of Caesium.

Caesium may be prepared by the electrolysis of certain of its compounds.

Properties of Caesium.

Caesium is a soft, silvery-white metal ; the most electro-positive one known. It forms a large number of known salts. Most of them are soluble in water and they show a strong tendency to form double salts. They resemble closely the compounds of rubidium and in a general way those of potassium.

A Few Compounds of Caesium (with elements already discussed).

With chlorine;	Caesium chloride, $CsCl$		
With oxygen;	(no oxide isolated)	Caesium hydroxide,	$CsOH$
With sulphur;		Caesium sulphate,	Cs_2SO_4
With nitrogen;		Caesium nitrate,	$CsNO_3$
With carbon;		Caesium carbonate,	Cs_2CO_3

RUBIDIUM; Rb; 85,43.

Introduction — Distribution, preparation, and properties of rubidium — Compounds of rubidium.

Data for Reference.

Density of solid rubidium, 1.52 (water being the standard = 1).

Fusing point of solid rubidium, 38.5° C.

Rubidium was discovered by R. W. Bunsen in 1860.

The name rubidium is derived from the Latin word *rubidus*, dark red (the reference is to the red lines in the spectrum afforded by compounds of rubidium).

Introduction,

The circumstances leading to the discovery of rubidium (and of caesium) are referred to under caesium.

The salts of rubidium (and of caesium) exist in nature in such small quantities and, moreover, resemble potassium and sodium salts so closely, that they would probably never have been detected except for the invention of some such exceedingly delicate method of analysis as spectrum analysis.

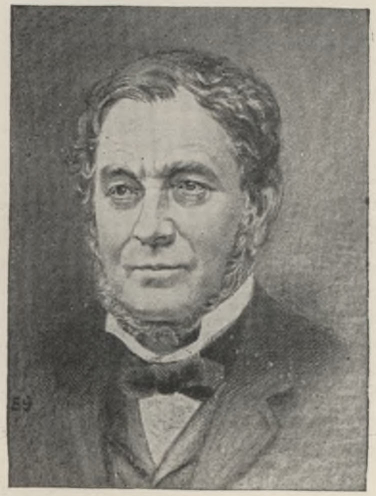
Distribution of Rubidium.

A thorough examination of the ashes of certain plants has shown that caesium and rubidium are considerably diffused over the earth in soils, although in small quantities. Thus, compounds of these metals have been detected in the ashes of certain vegetable substances, as coffee, tobacco, beets, grapes.

While certain widely distributed vegetables, as tobacco, for instance, take caesium and rubidium salts from the soil, these latter compounds cannot replace potassium salts as food for all plants, the caesium and rubidium compounds acting unfavorably on vegetable growth, while the potassium compounds act favorably.

Preparation of Rubidium.

Metallic rubidium may be obtained by heating certain compounds of the metal with carbon ; or by electrolysis.



Robert Wilhelm Bunsen, b. Göttingen, 1811; with Kirchhoff, the inventor of the spectroscope.

Properties of Rubidium.

Rubidium is a silver white metal, its color slightly tinged with yellow. In its chemical and physical relations, it corresponds most closely with the metal caesium, and, in general, with the other metals of the alkali group. It is strongly electro-positive.

It forms compounds analogous to those of the other alkali metals. Thus it produces alums corresponding in general with commoner and more well known alums.

A Few Compounds of Rubidium (with elements already discussed),

With fluorine;	Rubidium fluoride, RbF	
With bromine;	——— bromide, $RbBr$	
With chlorine;	——— chloride, $RbCl$	
With iodine;	——— iodide, RbI	
With oxygen;	(no oxide yet isolated)	Rubidium hydroxide, $RbOH$
With sulphur;		Rubidium sulphate, Rb_2SO_4
With nitrogen;		——— nitrate, $RbNO_3$
With carbon;		——— carbonate, Rb_2CO_3
		——— hydrogen carbonate, $HRbCO_3$
With silicon;	Rubidium silico-fluoride, Rb_2SiF_6	

COPPER; Cu; 63,60.

Introduction — Distribution, preparation (by mechanical processes, by wet processes, by dry processes, after preliminary roasting), properties, uses, and compounds of copper.

Data for Reference.

Density of solid copper, 8.36 — 8.95 (water being the standard = 1.)

Fusing point of copper, about 1100° C.

Copper has been known from very early times.

The word copper is derived from the Greek word Κύπρος (*Cypros*) Cyprus. (The word refers to the island in the Mediterranean, from which large quantities of the metal were obtained by the ancients.)

Introduction.

Copper has long been known as a useful metal. The ancients employed it in a state of greater or less purity in what is called bronze. In modern times, it has been produced on a large scale and employed for a multitude of purposes.

One reason why it has so long been used is found in the fact of its wide distribution; again it often occurs in the free and uncombined condition called native copper; finally its ores are comparatively easy of reduction to the metallic form.

Distribution.

Copper ores are widely distributed over the earth. But while a given place may have a rich deposit, another may have a deposit too lean to pay for working; in a given place, there may be a single ore prevailing or there may be a mixture of ores.

The following are a few of the principal ores of copper:

1 — Native copper.

2 — Cuprite, Cu_2O.
3 — Melaconite, CuO.
4 — Malachite, $CuCO_3 \cdot CuO_2H_2$.
5 — Azurite, $2CuCO_3 \cdot CuO_2H_2$.

6 — Copper glance, Cu_2S.

7 — Chalcopyrite, $Cu_2S \cdot Fe_2S_3$.

8 — Bornite (erubescite), $3Cu_2S \cdot Fe_2S_3$.

9 — Tetrahedrite (gray ore; fahl ore), $4(Cu_2S \cdot FeS \cdot ZnS \cdot AgS \cdot PbS)(Sb_3S_3 \cdot As_2S_3)$.

The United States has four important ore sections:

1st — The Atlantic coast region. The ore is chiefly chalcopyrite; it is mostly burned for the manufacture of sulphuric acid — its copper being a subsidiary product.

2d — The Lake Superior region. The ore is native copper; it extends over a narrow belt, one hundred miles in length. The deposits are said to contain on the average ¾ to 1¾ per cent. of metal (but the Calumet & Hecla deposits contain about 4½ per cent). These mines are worked at a large profit; they are often carried to a great depth — 4,000 feet.

3d — The Rocky Mountain region. The most important deposits are worked at a single point: Butte, Montana. The ores brought to the smelting works are said to contain from 6 to 10 per cent. of metal. While they are sulphuretted, they contain silver and traces of gold. (The ores of Gilpin, Colo., carry silver to the extent of 1 per cent. of all ore.)

4th — The Southern carbonate region. The most important workings in this region are in Arizona. The ores are of considerable variety of composition, but in many cases they carry arsenic and antimony, a circumstance which increases the cost of working.

The United States produces more than half the world's output of copper. Its principal sources are the sulphuretted ores of Butte, Montana, the native copper of the Lake Superior region near Houghton, Michigan, and the sulphuretted ores (often containing arsenic and antimony) of Arizona.

The recent total product of the United States was derived as follows:

Montana	47.	per cent.
Michigan	31.	"
Arizona	16.5	"
All others, United States	5.5	"
	100.0	"

Outside the United States, the greatest producers are Spain and Portugal; next to these come Chile, Germany, and Japan.

Preparation of Copper.

From appropriate compounds of copper the metal may be easily separated in a more or less pure form. The following are a few of the methods:

1 — By heating either of the oxides in a suitable crucible with carbon.

2 — By heating either of the oxides in a current of hydrogen gas.

3 — By adding a certain metal, for example, iron or zinc, to an aqueous solution of a suitable salt of copper.

4 — By electrolysis of a suitable solution of a salt of copper.

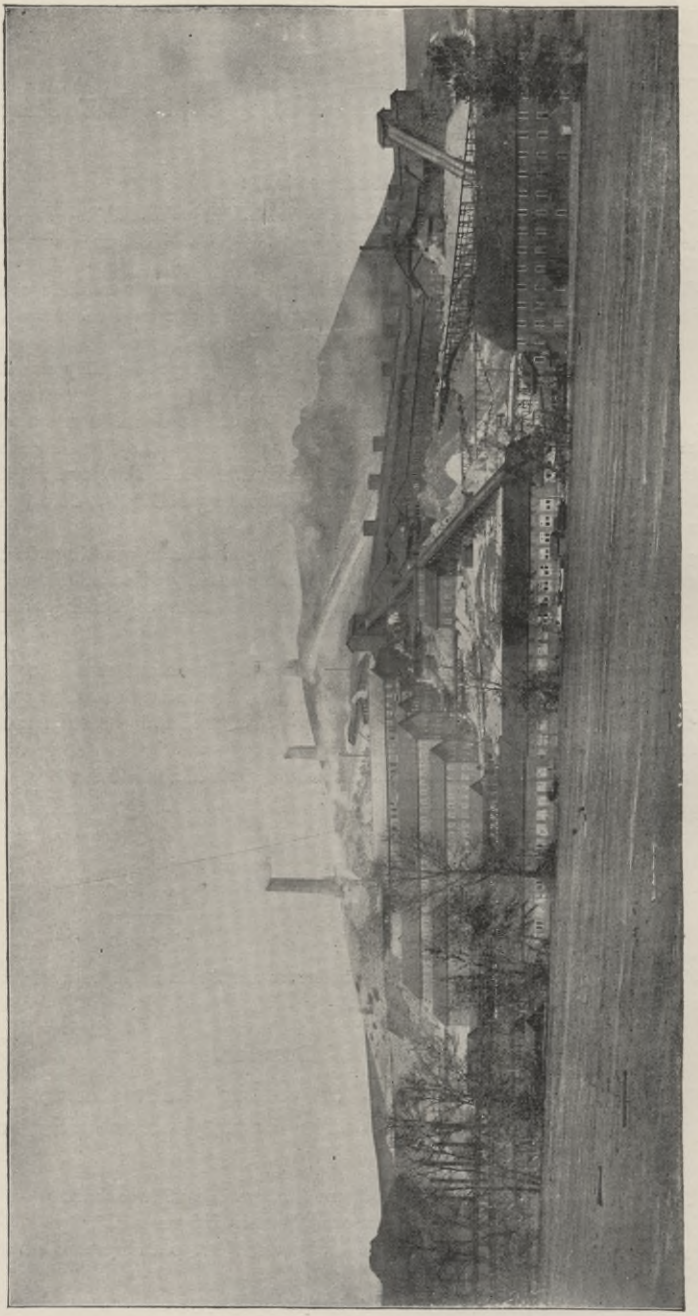


Fig. 29. A portion of the copper works at Anaconda, Montana. Underground flues from the works lead to the chimneys on the summit of the hill. The air is clouded with smoke. The area in the foreground is produced by filling a hollow with slag.

Metallurgic Extraction of Copper.

The total quantity of copper in the terrestrial globe is relatively very small; again, most of the convenient deposits contain relatively small amounts of the metal; but its chemical and physical properties make it so useful that somewhat expensive processes of extraction are practicable. They are classified as mechanical processes, dry furnace-processes (including roasting and fusion processes), wet processes (including the leaching of poor ores). In different places different processes are employed. That selected for use in a given case, depends upon the kind and quantity of ore, the cost of fuel, water, labor, etc.

In the case of copper (as with gold and silver) the ore is often worked at a mill which is at a distance from the mine, and it may be under different management. Thus in Montana the ores are mined at Butte, but the larger portion of them are smelted at Anaconda, or at Great Falls (in both places water and fuel are cheaper than at Butte); some are sent to the eastern part ot the United States — some have been sent even to Europe.

Swansea, in Wales, is an important smelting point; ores from Chile and from the Iberian peninsula are largely smelted there.

In practically all cases the ore from the mine is *concentrated;* that is, it is sorted by mechanical processes so as to get rid of worthless rock as far as practicable. Then the first-class ore is worked.

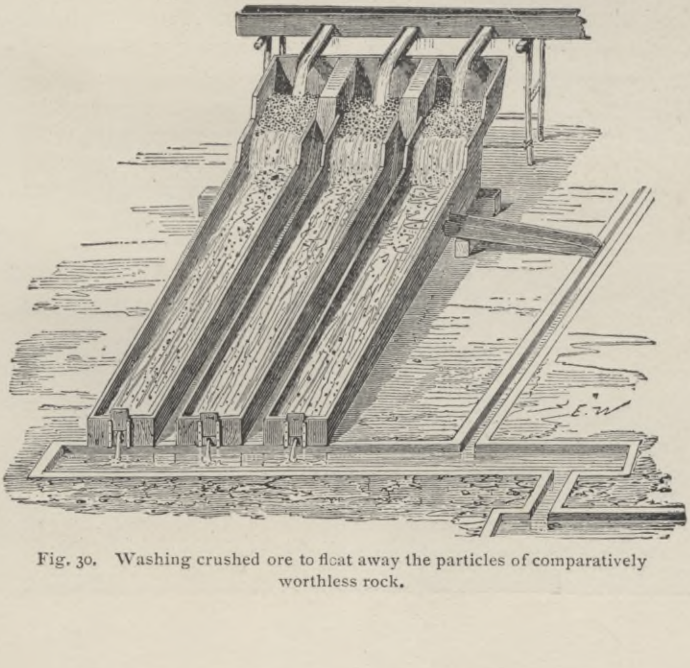


Fig. 30. Washing crushed ore to float away the particles of comparatively worthless rock.

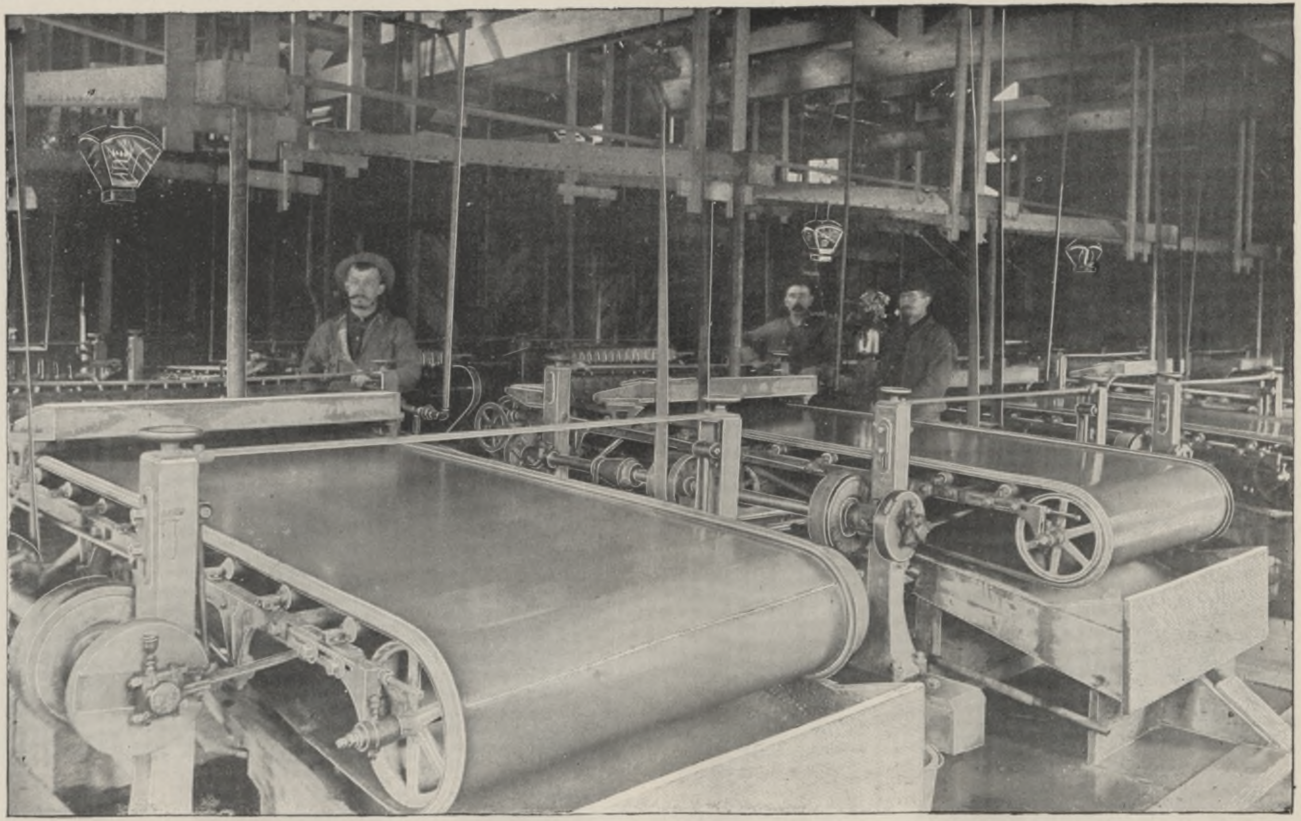


Fig. 31. "Vanners" for concentrating ore. Powdered ore and water are deposited evenly on the belt; the latter moves slowly from the spectator and slightly *upward;* the machinery gives the belt a side-shake also. As a result the heavier and more valuable ore is carried forward with the belt, and *upward;* the lighter, and comparatively worthless rock, is washed in a direction *opposite* from that of the moving belt, and *downward.*

1st — Mechanical processes for extraction of copper.

These processes are applied solely to native copper; they are employed in the Lake Superior region.

The ore is broken in a stone-breaker; crushed and sifted to an even size; washed with water in suitable "jigging" and "vanning" machines. The comparatively worthless rock, which is of lower specific gravity, is washed away while the metallic copper is left. The latter is melted, and then cast into ingots.

2d — Dry processes for extraction of copper.

A — *Applicable to oxides and carbonates.* — The ores are fluxed with sand, lime, and coal. The heat decomposes the cupric carbonate yielding cupric oxide; the carbon reduces cupric oxide to metallic copper; now the silicon dioxide forms a fusible slag with iron oxide present; at the same time the lime enters the slag (forming calcium silicate) and keeps out copper oxide.

B — *Applicable to sulphuretted ores.* — Ores of this class are numerous and important; Their treatment amounts to a combination of various *roasting* and *smelting* processes. These are carefully selected and conducted, the aim being to free the ore from sulphur, iron, and other impurities and finally to reduce it to the condition of nearly pure metallic copper.

— The roasting may be conducted in open air heaps. Here the broken ore is distributed over a small fire of wood. Little by little, portions of burning pyrites yield heat enough (from the combustion of their own sulphur) to accomplish the roasting of successively added portions of pyrites. Large heaps of pyrites may be kept on fire for months. Portions of the copper and the iron (of the ore) are changed to oxide. Not the whole of the sulphur, however, is thus capable of removal.

— The roasting may be conducted in *stalls*. The *stalls* are a series of brick walls so adjusted as to form bins for the ore. They hold the ore in convenient position, and moreover the walls retain heat, thus favoring the process.

— The roasting may be conducted in *kilns*. The kilns have shelves (of stone or iron) so adjusted that the particles of ore are moved from shelf to shelf — getting nearer and nearer to the moderate fire.

— The roasting may be conducted in *cylindrical furnaces*. The Bruckner furnace consists essentially of a large horizontal cylindrical tube, so adjusted between the fire-place and the chimney, that the flames of the fire may pass through it. The furnace is made to revolve. Thus the ore in the cylinder, continually exposes new sides to the air, and to the hot gases of the fire.

— The roasting may be conducted at *works manufacturing sulphuric acid.* At such works, iron pyrites may be used; but those containing even a small amount of copper are preferred (especially as they generally contain small quantities of silver and gold that may be extracted later). The ore, broken to a proper size, is burned on grates, in properly constructed furnaces, somewhat as coal is burned. The sulphur is changed to sulphur dioxide, which is afterward made into sulphuric acid; the ashes are treated as a roasted copper ore.

In these roasting processes the ore is not allowed to fuse. The prime intention is to expel sulphur (and arsenic and antimony) as gases and vapors by a thermolysis of the metallic sulphides.

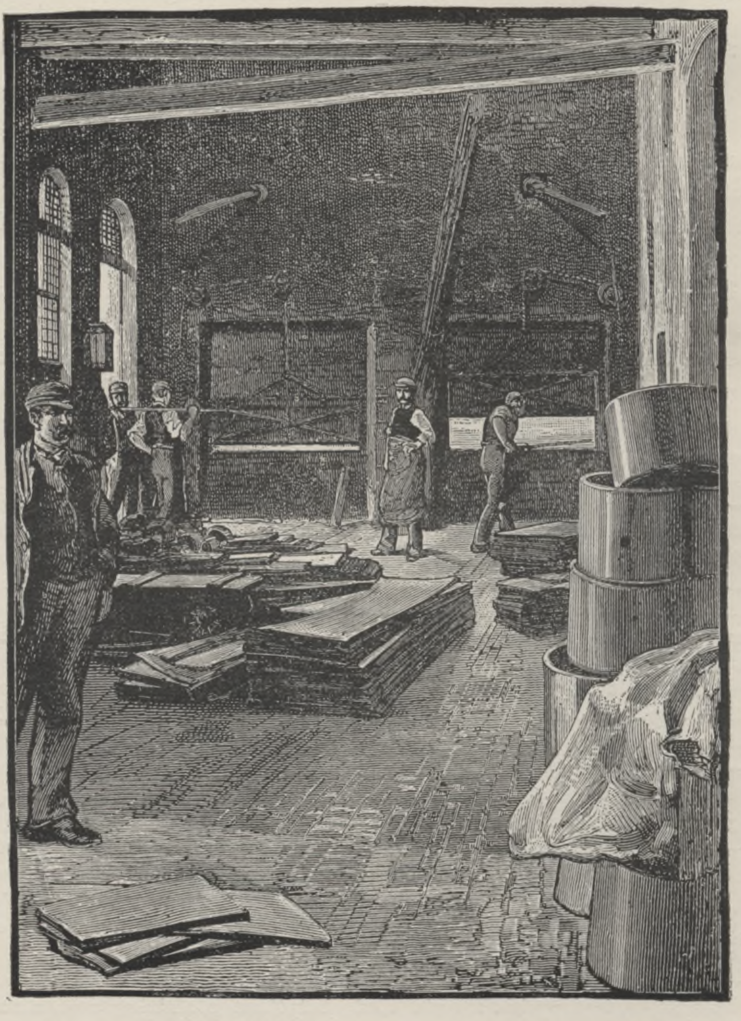


Fig. 32. Reverberatory (horizontal) furnaces for melting copper.

Of course, at least a part of the sulphur generally oxidizes to sulphur dioxide, SO_2, and escapes as a gas. At the same time portions of the metals undergo oxidation.

The smelting processes, as the name indicates, demand fusion. They produce a very complex series of chemical changes. They accomplish removal of sulphur by an oxidizing operation rather than by thermolysis. For example, after roasting, a given ore may yield ashes containing among other things copper oxide and ferrous sulphide; now upon smelting, the substances react so that the oxygen and sulphur (in part at least) unite and form sulphur dioxide, SO_2, a part of which escapes as a gas; again the interaction of these two substances, puts the iron into a condition favorable to removal;

$$2CuO + 2FeS + O = 2CuS + Fe_2O_3$$

Now the silicious matter present, readily combines with the ferric oxide forming a very fusible glass-like slag, ferric silicate; it is removed by skimming.

During fusion another very important reaction between cupric sulphide and cupric oxide yields metallic copper, the chief product sought:

$$2CuO + CuS = 3Cu + SO_2$$

As a result of the smelting operations, following roasting, the proportion of copper, in the material under treatment, is rapidly raised (by reason of sulphur expelled as gas and by reason of iron skimmed off in the slags formed); again toward the end of the process metallic copper is liberated.

Bessemerizing is a peculiar kind of second smelting. A portion of roasted ore is subjected to a first smelting; then the still melted "matte" is drawn into a Bessemer converter; a blast of air is driven through the "melt"; it is highly oxidizing and it burns out practically all of the sulphur, — the "melt" being maintained in a fused condition by the heat yielded by the combustion of this sulphur. The product when poured from the converter is cast into anodes for subsequent electrical purification. (See Bessemer processes for steel; also electrolytic purification of coarse copper.)

First general method.

In general, then, to produce copper from sulphuretted ores, the following series of operations is conducted (with more or less variations according to the conditions prevailing):

1 — The ore is broken to the desired size.

2 — It may be "concentrated" by some kind of washing.

3 — It is roasted.

4 — It is smelted. Either a *blast furnace* (having a "water-jacket" to prevent the walls from melting down), or a reverberatory (horizontal) furnace, or a Bessemer converter, may be used. In any case the impurities are furthur removed by the skimming of the slag.

5 — The roasting, smelting, and skimming of slag may be repeated, until finally a practically pure copper is obtained.*

Second general method.

In certain cases the conditions make a shorter course practicable. It involves the processes 1, 2, 3, 4, specified in the first method. But following these, the "matte" or coarse metal may cast into thick plates suitable for use as "anodes" in an electrolytic tank.

The tank is first filled with a water solution of cupric sulphate. In it are suspended both the coarse "anodes" and a set of thin and pure copper "cathodes." The electric current being now applied there results a gradual solution of the copper of each anode and its deposition upon the cathode until the latter is thickened up with copper. The cathode so deposited is of very high purity: it may be melted and cast into ingots for sale.

The demand for copper for use in conducting electricity, can be satisfied only by metal of a very high degree of purity (a small amount of impurity greatly increases the electrical resistance). But electrically deposited copper is very pure.

In connection with the electrolytic deposition of copper, as just described, a most important incidental circumstance develops: the gold and silver (which were in but minute quantities in the original ore and in the copper anodes) are liberated as fine powder which falls to the bottom of the tank. It forms there a "slime" which may be collected, melted, and cast into ingots. Since vast quantities of copper anodes are worked up, precious metal which could not be economically secured by any other process can be saved by the one in question.

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*A nearly purified copper is often subjected while melted, to a process called "poling," that is, the melted material is stirred with a pole of young unseasoned wood. The wood undergoes decomposition, giving out gaseous compounds of carbon, oxygen, and hydrogen, which produce violent agitation of the molten mass. As a result, impurities are brought to the surface, oxide of copper existing in the mass is decomposed, and a general improvement is accomplished.

3d — Wet processes for extraction of copper.

Leaching processes. — There are many copper ores that contain the metal in quantity too small to admit of successful working by the fusion processes detailed. Several wet processes have been devised with a view to securing the copper in a less costly way.

They may be stated in brief as dependent upon the following operations: *First*, the ore is roasted with common salt. This turns the copper into a soluble chloride, $CuCl_2$. *Second*, the roasted mass is treated with water, whereby the cupric chloride is dissolved. *Third*, to the water solution, scrap-iron is added. This precipitates the copper in the form of metal, in spongy masses. Such copper may be removed from the liquid, melted, and cast into ingots.

Properties of Copper — Physical Properties.

First, its toughness enables it to be beaten out into thin but strong sheets. These may be employed in making copper vessels for a multitude of domestic and manufacturing purposes. *Second*, its ductility is such that it may be drawn out into fine wire. Such wire is largely used for mechanical purposes. *Third*, the conducting power of copper for electricity is surpassed only by silver. Vast quantities of copper wire are now employed in electrical appliances. *Fourth*, copper is easily precipitated by the process known as electrolysis. Not only are there many uses of copper in connection with electrotyping — that is, in in the preparation of plates to be used for printing — but further, the electrolytic process enables copper to be precipitated upon other metals with great ease and in a compact form.

Properties of Copper — Chemical Properties.

First, copper readily unites with other metals to form important alloys. Copper and zinc produce brass; copper, zinc, and tin, produce bronze; copper and nickel produce German silver; copper and aluminium produce aluminium bronze. Many other alloys of copper are known and utilized. Those mentioned have most important uses owing to their physical and chemical properties. *Second*, copper combines with a great many non-metals and forms a great number of important compounds. It forms two notable series of compounds — the cuprous and the cupric.

The relations of a portion of copper to oxygen when exposed to the atmosphere, are interesting; it acquires a thin skin of oxide which stops further corrosion; thus, the chief portion of the metal is unaffected. On the other hand when an iron object oxidizes in the atmosphere, the oxidation progresses *under* the surface so that eventually the entire object becomes a mass of rust.

A Few Compounds of Copper (with elements already discussed).

With hydrogen;	Cuprous hydride,	Cu_2H_2		
With fluorine;	Cuprous fluoride,	Cu_2F_2		
	Cupric ———	CuF_2		
With chlorine;	Cuprous chloride,	Cu_2Cl_2		
	Cupric ———	$CuCl_2$		
With bromine;	Cuprous bromide,	Cu_2Br_2		
	Cupric ———	$CuBr_2$		
With iodine;	Cuprous iodide,	Cu_2I_2		
With oxygen;	Tetra copper oxide,	Cu_4O		
	Cuprous ———	Cu_2O		
	Cupric ———	CuO;	Cupric hydroxide,	CuO_2H_2
	Copper dioxide,	CuO_2		
With sulphur;	Cuprous sulphide,	Cu_2S;	Cuprous sulphite,	Cu_2SO_3
	Cupric ———	CuS;	Cupric sulphate,	$CuSO_4$
With selenium;	Cuprous selenide,	Cu_2Se		
	Cupric ———	$CuSe$		
With boron;	Cupric boro-fluoride,	$CuF_2\cdot 2BoF_3$		
With nitrogen;	Cupric nitride,	Cu_3N;	Cupric nitrate,	$Cu(NO_3)_2$
With phosphorus;	Di-copper phosphide,	Cu_2P_2;	Cupric phosphate,	$Cu_3(PO_4)_2$
	Tri-copper ———	Cu_3P_2		
With arsenic;			Cupric arsenate,	$Cu_3(AsO_4)_2$
			——— arsenite (Scheele's green)	$HCuAsO_3$
With silicon;	Cupric silico-fluoride,	$CuSiF_6$;	Hydrogen cupric silicate (dioptase)	H_2CuSiO_4

Cupric oxide, CuO, is a black solid, insoluble in water but easily soluble in the ordinary acids. It is easily produced by the heating of many copper salts, by which operation the acid anhydride is expelled. When vessels of sheet copper are highly heated, a coating of cupric oxide forms.

Cuprous oxide, Cu_2O, is a red substance. It is easily obtained by precipitating an alkaline solution of copper with grape sugar and certain other organic matters. It is often seen on the outer surface of sheet copper as sold by the coppersmith.

Blue vitriol, cupric sulphate, $CuSO_4\ 5H_2O$, is the commonest compound of copper used in the arts. Owing to its extensive uses, it is prepared in large quantities. In many establishments where copper is intentionally or accidentally "corroded," as in certain smelting works, a cupric oxide in a somewhat impure condition is produced and sold. This substance is subsequently dissolved in sulphuric acid. From the solution so produced, crystals of cupric sulphate are formed.

Paris green and *Scheele's green* are substances containing arsenic as well as copper. A green substance having the formula $CuHAsO_3$ may be produced by adding a solution of potassium arsenite to cupric sulphate. This is approximately the way Paris green is produced. Paris green is very largely employed in the United States as an insecticide in agriculture. Sprinkled on plants infested with injurious insects, it poisons the latter and so protects the crop.

Fig. 33. Running melted bronze (an alloy of copper, zinc, and tin) from the furnace to the mold.

SILVER; Ag; 107, 92.

Introduction — Distribution, preparation (the amalgamation, the Mexican, the Washoe, the barrel amalgamation, the smelting processes), properties of silver — Compounds of silver, especially the chloride, bromide, iodide, and nitrate — Uses of silver.

Appendix — The Comstock lode.

Data for Reference.

Density of solid silver, 10.42 — 10.57 (water being the standard = 1).
Fusing point of solid silver, about 1000° C.
Boiling point of liquid silver, 1400° — 1600° C.
Silver was known by the ancients.
The word silver is of early origin, its derivation not definitely made out.

Introduction.

Silver has been known from very early times; it is referred to in the Scriptures; it was employed by the ancient Greeks and Romans; it was studied carefully by the alchemists, incidental to their efforts to turn base metals into precious metals. Among the reasons why it has long been known are the following, *first*, it exists free and uncombined in the earth; *second*, it is easily obtained by simple smelting processes applied to its ores; *third*, it has many excellent properties which fit it for use in coins, medals and ornaments.

In 1871, Germany demonetized silver (commencing the sale of her stock in 1873); other nations took a somewhat similar course. Following these circumstances and others like the discovery (made about 1873) of the extraordinary deposit of silver ore known as the "Big Bonanza," in the Comstock lode in Nevada, and later of other important deposits in the United States, and the development of new processes for very complete extraction of silver, even from relatively poor ones, the market price of the metal has greatly declined. For several centuries, one ounce of silver had an average market price at the rate of *about* $1.2929 in gold coin; at present, one ounce of silver is sold at the rate of *about* 60 cents in gold coin. (This expression is not very different from the following: for a long time previous to 1873, one ounce of gold was exchangeable for *about* 16 ounces of silver; at present, one ounce of gold is exchangeable for *about* 32 ounces of silver.)

Distribution of Silver.

The following list includes a few of the most important minerals containing silver (but they exist in relatively small quantity):

Native silver, Ag,
Kerargyrite (horn silver), $AgCl$,
Argentite (silver glance), Ag_2S,
Stromeyerite (silver copper glance), $(AgCu)_2S$,
Pyrargyrite (ruby silver), Ag_2SbS_3,
Stephanite, Ag_5SbS_4,
Polybasite, $(AgCu)_9(SbAs)S_6$.

These minerals are of definite composition and relatively rich in silver.

— Most of the output of silver comes, however, from relatively poor ores — incidental it may be to the extraction of other metals, especially lead and copper. Thus silver is found associated with all lead ores, and a great many silver extraction works first secure lead and silver together, and then separate the silver. In

Fig. 34. Arrastra, used in the first stages of the Mexican process, for pulverizing silver ore.

Fig. 35. Mexican patio. **A mixture of silver ore, salt, sulphates, and mercury,** trodden by mules leads to a decomposition of the ore and to an absorption of the silver by the mercury.

many cases, silver occurs in pyrites containing considerable quantities of copper and small amounts of gold and silver. In such cases, the ores are roasted and are subsequently worked for all three metals.

—Silver is almost invariably associated with gold in natural sources of either metal; in a given ore, either the one or the other metal may be present in the larger quantity.

—Minute quantities of silver (and of gold) exist in sea water, and attempts have been made to secure these metals. At present, however, silver is more cheaply obtained from ores.

Preparation of Silver.

Silver may be prepared in the laboratory from many of its compounds and by many methods. A few are given.

1 —Almost any compounds of silver may be fused in a crucible with some suitable "flux" such as borax or sodium carbonate or a mixture of them; metallic silver separates and falls to the bottom of the fused mixture.

2 — Many aqueous solutions of salts of silver are decomposed when organic substances are added, the silver appearing as a dark colored powder at the bottom of the vessel or sometimes as a lustrous mirror on its walls.

3 — Most aqueous solutions of salts of silver are decomposed when zinc or certain other metals are introduced. The silver is precipitated.

4 — Most aqueous solutions of salts of silver are easily decomposed by electrolysis — the metal appearing at the cathode either as a lustrous coating or as a dark granular deposit.

Metallurgic Extraction of Silver.

Several essentially different kinds of processes are employed for the extraction of silver from ores.

First: The amalgamation process. — This process is applicable to ore which contains free and uncombined silver. The ore is pulverized with mercury. The mercury gathers the silver to itself. The amalgam of mercury and silver is subjected to distillation; whereupon the mercury goes off in vapor and is condensed for subsequent use, while the silver is left in the retort.

Second: The Mexican or patio process. — This process has long been used with great success in Mexico and South America for the extraction of silver from ores containing the metal as sulphide. It is worked somewhat as follows:

The ore is broken into moderate sized lumps in a suitable mill.

The broken ore is ground to a fine powder in a contrivance called an *arrastra.* It is a small crude mill worked by mules who drag heavy stones over the wet ore in a circular mortar-like space. (Sometimes a small amount of mercury is mixed with the paste.)

The pulp from the *arrastra* is transferred to the *patio.* The latter is a large paved courtyard, in the open air. To the pulp is added, at the proper times, common salt, iron and copper pyrites roasted to sulphates, metallic mercury, and it may be other substances. The mass is long and thoroughly trodden under foot by groups of mules. The chemical operations are complicated, but the process is remarkably efficacious in transferring the silver and gold to the mercury.

The material from the patio is removed to a "settling" tank and washed with water: the earthy substances are washed away and the amalgam is left. Later it is distilled.

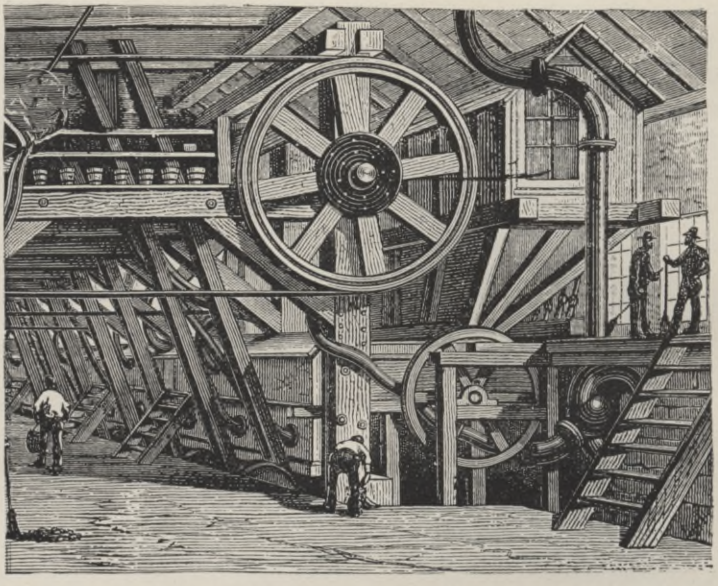

Fig. 36. Nevada mill using Washoe process for silver ores. The broken ore is received into bins (at the right); thence it is powdered under the stamps (in the centre); thence it is transferred wet by means of hose to the "pans."

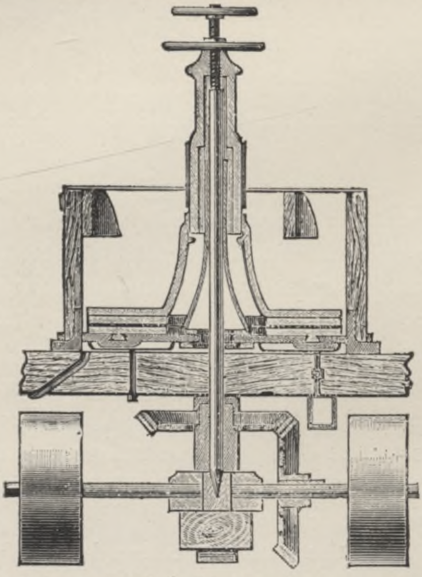

Fig. 37. "Pan" used in Nevada mills in the Washoe process for silver ores.

Third: The Washoe process (the modern pan amalgamation process). — This process was devised in Nevada where it has been employed with great success upon the sulphuretted ores of the Comstock lode.

— The ore is first crushed wet in the stamp mill, then passed over amalgamated copper plates (to catch the free gold or silver as soon as possible), then passed into tanks to deposit.

— The mud in the tanks is transferred to the "pan," a cylindrical iron tub. In the pan is a heavy *muller* — a circular steel plate — capable of revolving flat against the bottom of the pan, or while raised to any convenient point above it. The pan has a hollow bottom into which steam may be passed.

At first, the muller is set to grinding the ore yet finer. In due time mercury is added, the muller is raised, and stirring rather than grinding is carried on. Next substances like copper sulphate, salt, etc., are added. (In some cases the ore is dry-crushed and then roasted with salt, before transfer to the pans.)

— The paste from the pan being transferred to the "settlers" — iron tanks somewhat like the pans only larger — water is added and the whole stirred. The purpose here is to get the mercury, with its gold and silver, to run into a coherent mass.

— The amalgam from the settlers is placed in a tight iron kettle having a stout cloth diaphragm. By compressed air the mercury is strained through the diaphragm. The portion passing through (containing some gold and silver) is used in the pans again; the harder portion remaining in the bag is distilled in iron retorts. Mercury now vaporizes — it is condensed and used again. Gold and silver are left in the retorts — this bullion is melted in crucibles and cast into "bars."

— The ore from the settlers is run over vanners for "concentration" and subsequent further treatment for gold and silver.

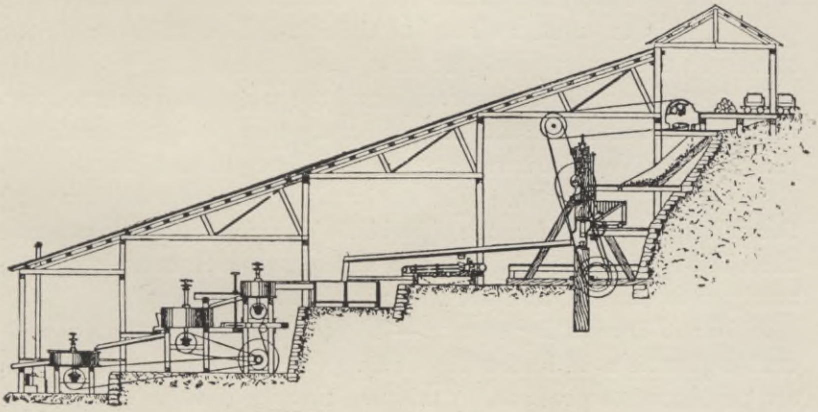

Fig. 38. Scheme of Nevada mill; Washoe silver process.

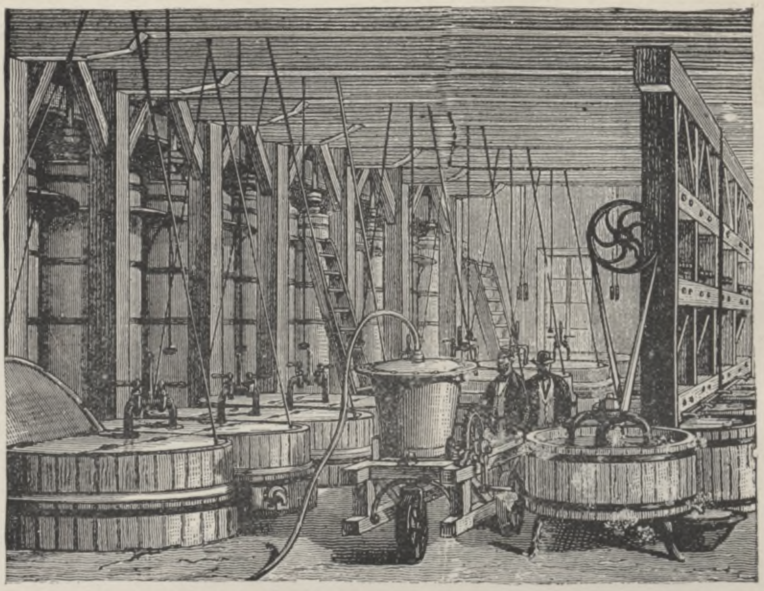

Fig. 39. Nevada mill; Washoe silver process.—The paste from the "pans" goes to the "settlers" (on the left); thence, the water and earthy matters go to the "agitators" (on the right); the amalgam from the settlers goes to the iron bucket (in the centre) to be strained.

Fourth: The barrel amalgamation process. — The ores, somewhat poor in silver, are roasted with common salt. If sulphur is present, it is expelled as sulphur dioxide. The chlorine of the salt turns the silver, partly, at least, to silver chloride.

Next the roasted mass is transferred to specially constructed barrels; at the same time mercury and scrap-iron are introduced into the barrels. Now the barrels are powerfully agitated by machinery. As a result the scrap-iron acts on the silver chloride, withdrawing the chlorine to form ferrous chloride. The free silver is at once absorbed by the mercury. When this process is completed, the amalgam is distilled and the silver is obtained.

Fifth: The smelting process. — Silver ores often contain considerable quantities of lead compounds. (In some cases lead ores are purchased to produce, by mixture, furnace charges of the type just referred to.) In these cases the ores are smelted just as if they were lead ores. The metallic lead obtained carries the silver with it; this product is called lead bullion.

The silver in the lead bullion is separated from the lead by immediate *cupellation*, or by Parkes' process, or by Pattinson's process (described later under *Lead*). But these latter processes result merely in affording richer alloys of lead and silver; in order to obtain the silver, they must be followed by the operation of *cupellation*. Of course, if the silver-lead, as produced at first, is sufficiently rich, cupellation may be resorted to immediately.

Cupellation is a process devised by the alchemists. It consists essentially in heating a mass containing lead, silver, and gold, in a covered furnace *provided with proper air currents*. The distinctive feature of the process is this: the oxygen of the air turns the lead into lead oxide, PbO; the silver (and gold) are left in a nearly pure state.

When conducted on a small scale by assayers, the *oxide of lead sinks into the bone-ash cupel* employed, leaving the gold and silver as a little *prill* of bullion upon the surface of the cupel.

When the operation is performed on a large scale, cupellation goes on much as described, only the cupel is very large and its bed is not intended to *absorb* the oxide of lead: a little gutter is provided, out of which this substance may flow. Moreover, more silver-lead is added from time to time until the amount of bullion left becomes as large as the capacity of the furnace will admit. Then the opera-

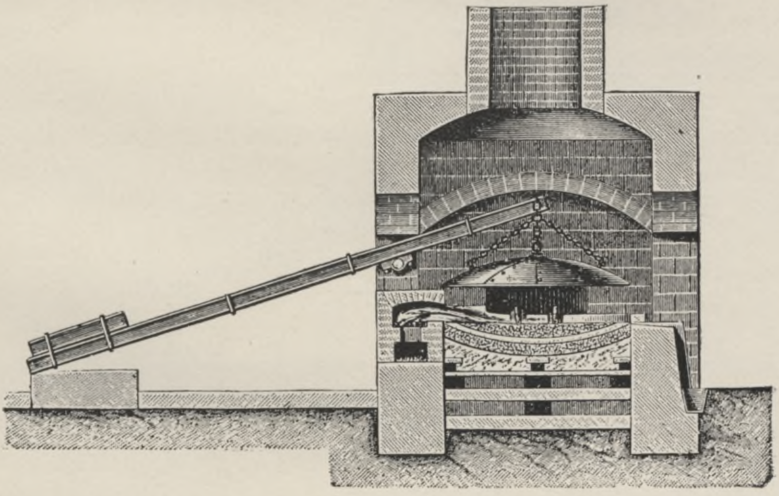

Fig. 40. Cupel furnace. The iron cover is counter-balanced by a weight. The fire, at the left, heats the bullion. The current of air, to oxidize the lead, enters by two tuyeres from behind the plane of the picture.

tion is stopped. The mass is allowed to cool, the iron cover of the furnace is removed and the bullion is withdrawn.

The oxide of lead obtained by this method is called *litharge* in commerce. It is much used in certain metallurgical operations. When produced on a large scale, it sometimes carries silver with it; in which case, the silver is occasionally secured by an additional operation.

Properties of Silver.

— Silver has a peculiarly pure white color.

— It is very malleable and ductile.

— It fuses with comparative ease. At the temperature of the oxy-hydrogen blowpipe it may be changed to vapor — and so, distilled.

Molten silver has the remarkable property of absorbing oxygen gas; liberating it, however, upon subsequent cooling. This property gives rise to the phenomenon of *sprouting*, often observed in the processes of cupellation; as the absorbed oxygen leaves the cooling silver it throws up minute fibres of silver upon the surface of the mass. The term "vegetation" is applied to this product on account of its appearance.

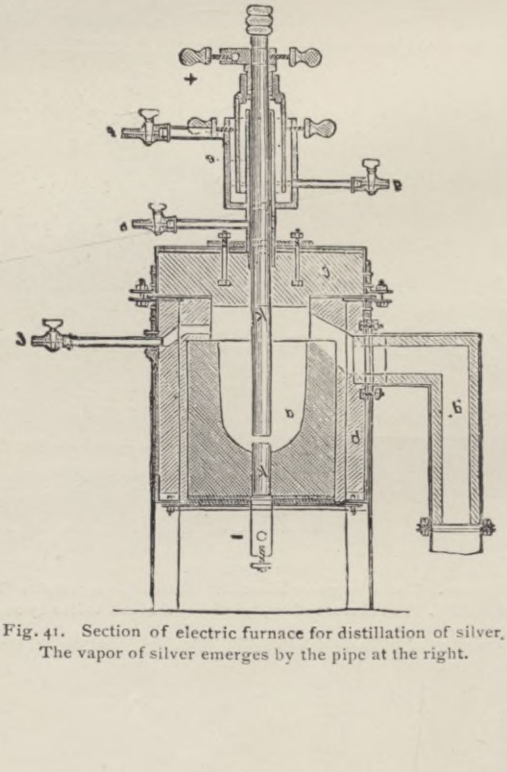

Fig. 41. Section of electric furnace for distillation of silver. The vapor of silver emerges by the pipe at the right.

— Silver is the best conductor of electricity known.

— Silver forms a great variety of compounds with other elements.

Many of them decompose and turn black under the influence of sunlight, especially in presence of organic matter. Under these circumstances the silver loses more or less of the other element or elements combined with it. For photography the most favorable compounds are the chloride, bromide, and iodide of silver.

Uses of Metallic Silver.

— Silver is very largely used in coinage. When alloyed with from seven and one-half per cent. to ten per cent. of copper, it still retains its beautiful white color and is yet hard enough to resist to a considerable extent that abrasion incident to wear which occasions serious loss in gold coins. The coins of the United States and of France contain ninety per cent. of silver and ten per cent. of copper. The coins of Great Britain contain ninety-two and one-half per cent. of silver and seven and one-half per cent. of copper.

— Silver is largely used for the better kinds of household utensils — what is called solid silver is not pure but is for this purpose also, alloyed with copper.

— Silver is largely used in electroplating. A sufficiently thick deposit of metallic silver upon ware of inferior metal, either brass or German silver, affords spoons and other articles for household use, every way as suitable as those of coin silver or sterling silver.

— Silver finds at present an enormous use in the manufacture of ornamental articles of every description. Either solid or silver plated goods such as card cases, match boxes, watch cases, the backs of hair brushes, ornamental pins, consume great quantities of silver.

— Silver is very largely used in the processes of photography. (While scraps of photographic paper containing silver are saved and burned and the silver recovered, yet considerable quantities of silver disappear from commerce in photographs which are preserved.)

— Silver is now used to some extent as a deposit upon glass for the preparation of mirrors ; it replaces the amalgam of tin and mercury formerly employed.

A Few Compounds of Silver.

With fluorine;	Silver fluoride,	Ag_2F		
		AgF		
With chlorine;	——	Ag_2Cl;	Silver chlorite,	$AgClO_2$
	—— chloride,	AgCl;	—— chlorate,	$AgClO_3$
With bromine;	—— bromide,	AgBr		
With iodine;	—— iodide,	AgI		
With oxygen;	Silver oxide,	Ag_2O;	Silver hydroxide,	AgOH
With sulphur;	Silver sulphide,	Ag_2S;	Silver sulphite,	Ag_2SO_3
			—— sulphate,	Ag_2SO_4
			—— hyposulphite,	$Ag_2S_2O_3$
With selenium;	Silver selenide,	Ag_2Se		
With tellurium;	Silver telluride,	Ag_2Te		
With nitrogen;	Silver nitride;	AgN_3;	Silver nitrate,	$AgNO_3$
	—— cyanide,	AgCN;	—— cyanate,	AgOCN
			—— sulpho-cyanate,	AgSCN
With phosphorus;			Silver phosphate,	Ag_3PO_4
With arsenic;			Silver arsenite,	Ag_3AsO_3
			—— arsenate,	Ag_3AsO_4
With carbon;		Ag_4C(?);	Silver carbonate,	Ag_2CO_3
		AgC(?)		
With silicon;	Silver silico-fluoride,	Ag_2SiF_6		

Silver chloride, AgCl, is easily produced by the addition of hydrochloric acid or a soluble chloride to a soluble salt of silver, for example, silver nitrate. This substance is of great importance in photography since it is very sensitive to the action of light. The chemical rays of light decompose silver chloride. They have a similar influence upon the corresponding iodide and bromide. In photography, the final paper print called the *positive*, is produced by the use of a preceding appliance called the *negative*.

This negative is produced in the camera by reason of light falling upon a transparent plate of glass, or celluloid or the like, coated with a film imbued with a salt of silver, e. g., silver bromide, AgBr. The negative is a sort of reverse picture: one in which the black parts of the object appear white or transparent and the light parts of the object appear dark and opaque. When the negative is placed upon a piece of *silver paper*, that is, paper having a thin film of egg albumen containing chloride of silver, the negative acts like a stencil. Upon allowing the sunlight to fall upon the combination, the chemical rays change the paper to a positive. This, after proper washing and other treatments, may be pasted upon cardboard, thus producing the modern photograph.

Silver nitrate, $AgNO_3$, is a white crystalline salt produced by dissolving metallic silver in dilute nitric acid. It blackens upon contact with organic matter, owing to the decomposition of the salt. It is sometimes melted and cast into rods, in which form it is used in surgery under the name of lunar caustic. It is somewhat used in medicine, but its chief consumption is in photography.

Appendix to Silver. — The Comstock Lode.

Printed matter relating to "the Comstock" is very voluminous. It comprises government reports, scientific volumes, court records of litigation, magazine articles, newspaper material, and even novels. The story of the lode — its first discovery; the chemical, metallurgical, and geological processes involved; the rude excitements of the mining camp that gathered in the wild and snowy mountains over it; the extraordinary litigations with respect to its claims and companies; the fabulous wealth secured by a few of its owners; the frenzied speculation in the shares of the many companies working it; the lowering of the market price of silver (incident in part at least to the great output of the Comstock), with the remarkable political disturbances that followed — have furnished ample material for many volumes.*

The term lode is applied in various ways, but chiefly to a notable vein of metal-bearing ore. The term "Comstock lode" is applied to a body of ore, chiefly silver ore, located in the extreme western part of Nevada, in Storey County, underneath Virginia City. It is east of the Sierra Nevada; about twelve miles from Washoe Valley. Here, in the midst of a cluster of mountains, valleys, and cañons, is Mt. Davidson, 7,827 feet high. Within the area having a radius of ten miles around this peak, were enacted the stirring scenes incident to the discovery and development of the Comstock deposits. The great lode runs in general north and south. It has a length of about 20,000 feet, and a width of from 100 to 1,200 feet. The vein has been followed downward to a depth, in some cases, of 3,000 feet. The deposit, in one portion

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* We give a few useful references:

Tenth Census of the United States (1880). Vol. XIII. G. F. Becker. The Precious Metals.

U. S. Geological Survey for the Fortieth Parallel (1870). Vol. III. (Eng. Dept. U. S. Army No. 18). Earlier History of the Comstock.

Bancroft, H. H. *History of Nevada, Colorado, and Wyoming.* San Francisco, 1890.

Shinn. C. H. *The Story of the Mine.* New York, 1896.

Popular Science Monthly, October, 1896.

Harper's Magazine. 22:145, 289. 30:681. 31:1, 151. (Articles by J. Ross Browne.)

of its underground development, appears to have been the richest pocket of ore of the precious metals that human beings are known to have found.

The valuable ores of the vein are chiefly as follows:

Native gold,
Native silver,
Kerargyrite (horn silver), $AgCl$,
Stephanite (antimonial silver sulphide), Ag_5SbS_4.

There are many other minerals distributed through the vein, some of them of little value, and some of them an impediment to the working of the ore. The principal minerals that are either comparatively worthless or objectionable are as follows:

Clay and barren rock,
Galena, PbS, (some of it argentiferous),
Stibnite, Sb_2S_3,
Zinc blende, ZnS,
Iron pyrites, FeS_2,
Chalcopyrite (copper pyrites), $Cu_2S{\cdot}Fe_2S_3$.

—The ore was at first worked for gold alone, by very crude "placer" methods (see chapter on Gold); as a result, the pioneers lost for a time the larger portion of the precious metals: that in the silver-bearing minerals. As soon as the fact was discovered that the chief values resided in the sulphuretted silver compounds, the miners groped about for better methods of working.

Soon they managed to invent the Washoe process, described already. This process, evidently suggested by the ancient Mexican patio process, was modified in certain particulars, from time to time, and by different individuals. Some attempted modifications were ridiculous; some were rational and useful. Ultimately the plan was developed into a definite and effective mode of procedure.

—In many places where mining is carried on, the earth and rock lying above the mine undergo serious settlement, owing to lack of support, where cavities have been formed by excavation. The difficulty is overcome by resort to a variety of expedients. Columns of worthless rock may be left in the cavities at proper points, or framework of stout timbers may be introduced. In addition, worthless broken rock may be back-filled between the pillars or timbers.

Fig. 42. Timber-work to support earth and rock overlying a cavity from which ore has been taken.

In the case of the Comstock, the overhead pressure was very great, owing to the depth of the workings. Again, the earthy material was very soft; this favored subsidence, and it also offered poor material for pillars. Ordinary timber work experienced two difficulties: in some cases the cavities were too large for practical overhead timbers, and often the thrust was so great that timber work introduced was twisted and displaced. In the early stages of working here, the precaution of back-filling waste broken rock underground was neglected. In some cases, most serious and dangerous cavings-in occurred, leaving great craters even on the surface.

At length a German, Philip Deidesheimer, invented a system of timbering which served. He made open rectangular frames called "square sets," out of 12-inch timber, squared and thoroughly mortised together. They were constructed in series of two or three uniform sizes. When placed underground they could be so packed together as to form a larger or smaller mass of framework, and to fit satisfactorily any cavity that it might be necessary to make. At first, the plan met with little favor, on account of its great expense, in a region where wood had to be cut on steep mountain slopes, and secured and worked at enormously inflated prices for every kind of labor; but eventually the system was widely and successfully adopted.

— Most deep mines are subject to accumulations of water at the lower levels; it has to be pumped out.

The Comstock mines experienced serious water inflows: often the water had a temperature as high as 170° F. (It has been computed that at a depth of four thousand feet the water will be found at the boiling temperature.) Some of the largest pumps in the world were constructed for the Comstock mines. The important enterprise known as the Sutro Tunnel was planned, and carried through (from 1865 to 1881, under very great difficulties), to drain off the underground water in the various mines of the lode. (It cost about two million dollars.)

— In most mines the general temperature of the galleries increases regularly with the depth. In the Comstock the heat — a remnant of the volcanic action which produced the lode — was exceptionally great.

In 1881 a test of the temperature, at every hundred feet, showed in a certain shaft the following results:

At 100 feet down	50½°
" 500 "	68°
" 1,000 "	81°
" 1,500 "	101°
" 2,000 "	111°

But in another mine the temperature at 1,700 feet was 140°. It was partly due to the influx of hot water; when the water was pumped out, the temperature dropped — but it was still 100° F In most of the Comstock mines the men though nearly naked could work only a few hours at a time; perspiration dripped into their shoes filling them to overflowing; often the picks were so hot that gloves were needed. The expense incident to supplying ice was a serious one for the mine owners.

— The most successful years of the Comstock lode were from 1874 to 1878 inclusive; later the output diminished very materially.

The aggregate yield of all the mines on the Comstock lode up to about 1881 is said to have been 306 million dollars, extracted from 7 million tons of ore. (Against this sum must be noted about 62 million dollars paid in in assessments by stockholders.) In the neighborhood of 118 million dollars was paid back in dividends. The enormous balance unaccounted for here, was distributed in expenses of construction, maintenance, salaries, labor (about 88 million dollars) and *sundries.* It is believed that the sundries account was one that would not bear very careful examination.

It is said that when the great bonanza partners were in the best years of their mining, Flood, O'Brien, and Fair each drew regularly $750,000 per month, and Mackay $1,500,000 per month. The total amounts drawn by the partners appear to have been: for Mackay, 120 million dollars, and for each of the others 60 million dollars.

The amounts given above are only approximate. It is stated that in the returns made for the purposes of tax assessors, the outputs of the mines were systematically and grossly underestimated.

Since the working out of the richest deposits of the lode, Nevada has fallen in rank as a silver-producing state. The output of the most productive sections of the United States is approximately as follows:

Silver production (year 1897) in Troy ounces. (Total U. S. over 56 million ounces):

Colorado	21 +	million ounces
Montana	16 +	"
Utah	6 +	"
Idaho	6 +	"
Arizona	1 +	"
Nevada	1 +	"

Condensed Historical Sketch of the Comstock.

1 — Some of the Mormons, who were making settlements in Utah between 1847 and 1850, claimed to have discovered the outcroppings of the Comstock. (What is now the state of Nevada was set off from western Utah.)

2 — Hosea Ballou Grosh and Ethan Allen Grosh his brother, are thought to have made a distinct and definite discovery of the Comstock lode between the years 1856 and 1857; but in the autumn of 1857 Hosea died, and in the winter of 1857 Allen died, the latter having his feet and legs frozen while making his way through the snow drifts of the stormy and nearly uninhabited Sierras.

3 — Early in 1859 a number of reckless prospectors, among them Henry T. P. Comstock, composed a small mining camp near where Virginia City now stands. They took out some gold, by the primitive methods of placer mining. They were annoyed by a heavy black material which they considered worthless; but which was subsequently shown to be a very rich silver ore. Later in the season, when a trustworthy assay revealed the nature of the "black stuff," a wild rush of California miners and prospectors set toward the region then known as "Washoe." In a few months twenty thousand unkempt and unwashed adventurers straggled and struggled into this windy and stormy region.

4 — From 1860 to about 1869 the Comstock lode was worked violently and brutally. As early as 1861, seventy-six mills, carrying in the aggregate 1,153 stamps, costing at least six million dollars, had been built. Where workers in one mine accidentally dug into the pits of adjacent claims, the men fought one another. (Some of the mine owners hired fighting men for the purpose. In some cases chemical weapons were employed: poisonous gases were driven into a neighbor's mine galleries, or smudges which gave forth acrid choking smoke, were employed to expel opposing miners from their works.)

While such Homeric struggles were going on deep underground, litigation was proceeding above the surface. The costs of legal proceedings, including bribery, corruption, and all manner of fraudulent processes, probably amounted to ten million dollars, or one-fifth of the entire product of the lode at this period.

5 — Between 1869 and 1879 the lode had its most remarkable experiences. Certain leading groups of men formed partnerships of one sort and another. They began to combine claims, mines, and mills, and to work the deposits in a more systematic manner. The most famous of these groups was that composed of Flood & O'Brien — liquor dealers in San Francisco — who had become

Fig. 43. Miners at the preliminary work of tracing the course of a vein of metal-bearing ore.

rich in mining speculations, and who entered company with two young, able, and intelligent Irishmen, James G. Fair and John W. Mackay.

In the winter of 1872-3 the mines of the firm were not doing well, but in March of 1873, while Fair was working underground and Mackay was superintending above ground, there came a marvellous change. Fair struck a thin vein of ore that appeared promising. "It was a narrow seam hardly thicker than a knife blade. He ordered the laborers to follow it inch by inch. They did so, even where only a film of clay showed where the thin streak had pinched out. After a while the slender clue was again picked up, and Fair and his workmen laboriously followed the dark line of silver sulphurets through the underground labyrinths for hundreds of feet." Fair became ill, and the drift, though managed by old and experienced miners, was run far east of the clue, while he was absent. The vein seemed to be lost, but Fair recovered, came back, and again picked up the thread of ore. Under the skilful guidance of this remarkable leader, who was known through the section as having "a fine nose for ore," the film was traced until it widened to twelve feet in thickness.

Under the most arduous labor it had been explored by October, 1873, at a depth of 1,167 feet, so that the width of the ore body was found to be 40 feet. October was a month of tremendous labor. A "big bonanza" had been found. A space 20 feet high, 54 feet across, 140 feet long, every inch of valuable ore, had been examined; at 1,300 feet below the surface, it seemed to have 300 or 400 feet of ore.

"By May, 1874, the scene within this imperial treasure-house was a stirring one. Masses of very expensive timber frame-work were piled up in well-jointed stages from basement to dome, 450 feet above, in cavities from which the ore had been extracted. Even then the enormous pressure of earth and rock above made the timbers rock, groan, and in some cases crush to kindling wood. The brawny laborers (stimulated by the enormous prices paid, in order to quicken the work before fire or some other accident should spoil everything) were clambering over the frame-work, tearing out the glittering ore, or descending and ascending in crowded cages. Flashes of exploding powder were blazing from the dripping walls of mineral. Pillars of smoke and gas filled the narrow drifts. Muffled roars echoed along the dark galleries. At all times a hail of rock fragments was rattling on the floors of the levels, or massive lumps of ore were falling heavily on the slanting piles at their feet. In some places, the sides of the huge cavern glistened as if set in silver, — not indeed silver, but crystals of iron and copper pyrites; in other places, great masses of blue and purple ore and gleaming crystals of quartz several inches long, chloride of silver, pale green or steel gray in color, or silver sulphurets, black and lustrous, dazzled the eyes. The general color of the material of the great deposit ranged however from bluish gray to deep black.

From 1873 to 1875 the feverish work of extracting the material of this great deposit went on in the presence of enormous difficulties. The forests of timber placed in the cavities needed constant care and renewal, for strong as they were the pressure above them was such that they were in danger of collapse. The whole mass might settle at any time, and make a ruin that could not be re-opened except by vast expense and years of labor. Mackay, keenly alive to the everpresent dangers of fire and collapse in the wood-work, left nothing to chance, but personally inspected the drifts night after night. His ceaseless vigilance had its reward, for no accident happened until the bonanza was thoroughly worked out. A few years later, however, serious and dangerous fires started in the abandoned levels, and though the greatest efforts were made to extinguish the flames, the timbers smouldered for weeks, and the drifts finally became unfit for passage, — a very labyrinth of traps and pitfalls, shunned by every miner to this day."

These lines refer chiefly to the underground work of the mines controlled by Flood, O'Brien, Fair, and Mackay; at the same time other firms were at work on their various claims, but with less good results. Their rivals looked upon the four partners now with jealousy, now with distrust, for while their work was going on with as much secrecy as possible it could not be entirely concealed. It is unnecessary here to go into any further details either as to the mining operations or as to the tremendous stock speculations these operations prompted.

While the main body of ore had been gotten out of the "Big Bonanza" deposit by the summer of 1875, the extraction of the *metals from the ore* continued to a much later date. Moreover other miners hoped to strike a similar deposit. But by 1879 the failure to discover important new deposits and the exhaustion of the old ones, and the spread of information, resulted in a stoppage of profitable work and a sudden and disastrous collapse of speculation in shares. Mining continued, and it is still in progress, but with very moderate results.

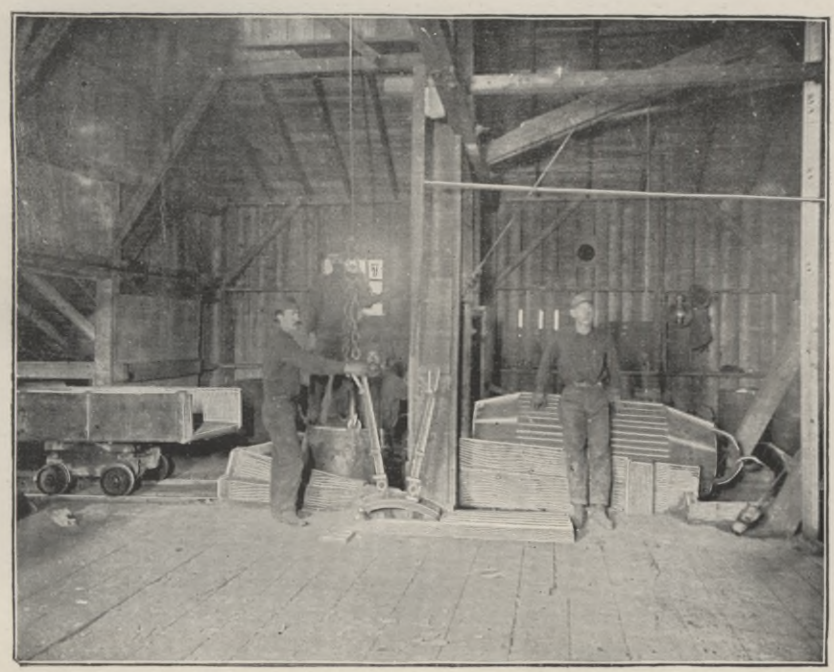

Fig. 44. House at the mouth ot a mine. The man at the left is preparing to lower a bucket. The man at the right leans against the plunger of a mine-pump.

GOLD, Au, 197.23.

Introduction — Distribution, preparation, extraction (placer mining, hydraulic processes, the milling process, chlorination, cyaniding, and other processes) properties, and compounds of gold, especially chloride.

Appendix — The chief gold producing districts of the world.

Data for Reference.

Density of solid gold, 19.3 (water being the standard = 1).
Fusing point of solid gold, about 1200° C.
Boiling point of liquid gold has been estimated to be about 2240° C.
Gold was known to the ancients.
The derivation of the word gold is uncertain.

Introduction.

The metal gold has been known and valued from the very earliest times: it is mentioned in the Scriptures and in other early writings.

The reasons for the antiquity of man's knowledge of gold and his appreciation of it are to be found in its mechanical, physical, and chemical qualities, of which the following may be mentioned:

First, its yellow color, which naturally attracts attention; *second*, the ease with which it fuses; thus, grains of it found in alluvial sands, can be melted together into masses by the use of very simple heating appliances; *third*, its malleability and ductility and the general ease with which it may be worked into ornamental objects; *fourth*, its lack of affinity for oxygen and certain other non-metals; to this particularly, is referable its existence in the free or uncombined form in quartz rock, as well as in alluvial earth; for this reason, also, the metal does not oxidize upon melting it; thus, there is less loss in the various metallurgical treatments of it; for this reason, in part, the grains run together in melting, as no oxide is formed to prevent such cohesion of melted grains; this same principle has rendered it valuable for coins and for trinkets: a coin of gold does not easily tarnish, but retains its beautiful metallic appearance: a gold ornament, too, does not become discolored.

Distribution of Gold.

Gold is very widely diffused through the mineral kingdom. It is present in practically all quartz rock. It is found in a great many other kinds of mineral matter.

1 — *It occurs chiefly in the form called native gold.* This term is intended to represent that the element is in the free or uncombined form.

It must be remembered, however, that the so-called native gold almost invariably contains silver associated with it, and often contains traces of iron, of copper, and occasionally of other metals, platinum for example.

The native gold of the highest quality found contains 99 per cent. of the metal; Australian gold averages from 96 to 96½ per cent.; Californian gold averages 87½ to 88½ per cent. (Klondike gold is less rich); in some cases, as in some German native gold, the precious metal occurs in as small proportion as 85 per cent.

2 — Gold occasionally occurs in the earth in chemical union with other elements; for example, as a gold telluride, called calaverite, $AuTe_2$

3 — Small quantities of gold exist in practically all iron pyrites and copper pyrites. The fact is certain, although a difference of opinion prevails as to the chemical condition of the gold: on the one hand it is thought to exist as minute particles of metallic gold distributed, it may be, in the inside of small masses of pyrites; on the other hand it is represented to exist in a state of chemical combination. At present it is impracticable to judge between the opposing views.

4 — Minute quantities of gold (and silver) appear to exist in sea-water.* Attempts have been made to secure it economically, but apparently without success.

At present the largest portion of the annual output of mined gold comes from the United States, South Africa, Australasia, and Russia. But contributions are furnished from the territory of nearly every nation.

Preparation of Gold.

In the laboratory, gold may be prepared from its salts — with especial ease indeed because of its weak chemical affinities — by ordinary processes like those detailed for preparation of silver. These are, in brief, fusion with fluxes; reduction by organic and other "reducing" substances; influence of uncombined metals like zinc; electrolysis.

If either oxalic acid, $H_2O_2O_2C_2$, an organic reducing substance, or ferrous sulphate, $FeSO_4$, an inorganic reducing substance, is introduced into a solution containing gold, the latter element begins almost immediately to separate in the metallic condition.

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*Liversidge, A. — *Chem. News*, 74: 166, 182. Also *Eng. & M. J.*, Nov. 21, 1896, and Dec. 19, 1896.

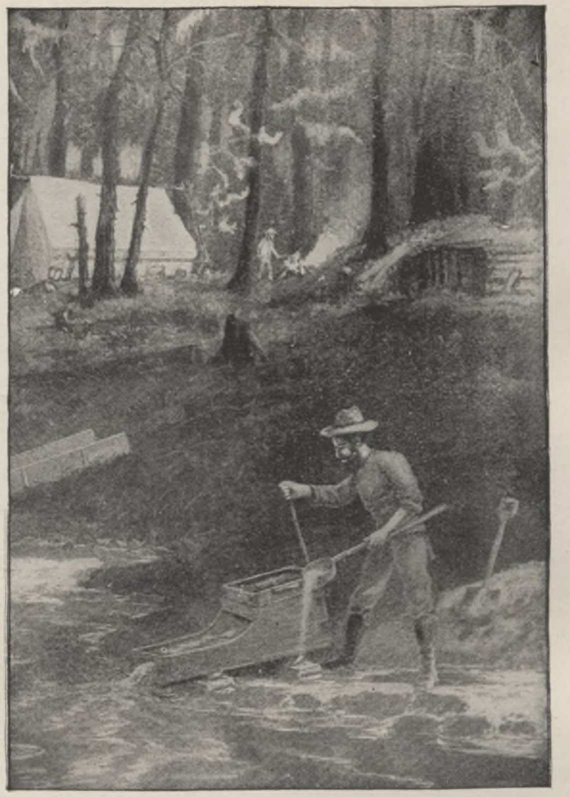

Fig. 45. Washing auriferous earth by means of the "cradle" or "rocker."

Metallurgic Extraction of Gold.

The processes employed for extracting gold from its mineral sources are very varied. They may be arranged for description in five groups: 1st, Placer mining; 2d, Milling; 3d, Chlorination; 4th, Cyaniding; 5th, Processes incidental to the extraction of other metals, as copper, silver, etc.

The process chosen for a particular case depends not only upon the character of the ore but also upon the relations of its site to water supply, fuel supply, transportation facilities, cost of labor, and the like. Moreover, in many cases more than one of the processes mentioned is applied to the ore, i. e., one process secures a certain portion of the gold present, then other processes, applied in succession, secure other portions.

Placer Mining.

This process is applicable to soft or loose deposits, like drift in the sands of river beds, etc. Though an ancient method it has been much improved in recent years.

It consists essentially in treating the loose soil with water in such a way as to wash away the lighter and less valuable mineral matter, and afterwards to secure the heavier "gold-dust" left.

The cradle method. — The primitive method of obtaining gold from the sands of rivers is by the use of a box on rockers, the contrivance being called a "rocker" or "cradle." The earth is shoveled into an upper sieve-like compartment of this box; then

Fig. 46. Sluice for washing auriferous earth in placer mining. (The men in the foreground are testing the earth by "panning.")

it is drenched with water, and the contrivance is rocked. The coarse material left on the sieve is rejected. The fine material passes through the sieve; but the lighter particles float away while the heavier gold-dust settles to the bottom of the lower compartment of the "rocker."

The sluice method. — This process, virtually an extension of the cradle method, was early introduced into California. It may be stated in brief as follows: A company of miners select a gold-bearing stream. At one side of it they build an elevated trench of wood beginning at some high point in the stream and extending for hundreds of yards to a low point. In the inside of the trench, at the bottom, they introduce little wooden bars called "riffle bars."

When this trench, called a "sluice," is ready, the water of the stream is diverted so as to flow through it. Then the miners, digging in the dry bed of the stream, shovel the gold-bearing sands into the sluice. After the current of water has carried away toward the end of the sluice the valueless earthy matter of the sands, the gold dust is found in the bottom of the sluice. Sometimes minute and thin leaves of gold are washed away with the earth. To prevent this loss, the end of the sluice is provided with a pool of mercury, or else a broad plate of copper amalgamated with mercury. Any floating particles of gold coming in contact with the mercury are quickly absorbed by it and afterwards secured by the miners.

Hydraulic mining. — This process represents an extension of sluice method. The hydraulic miner has a large and well constructed sluice. Sometimes the bottom is paved with round stones. He secures or constructs a reservoir of water upon some very high point adjoining the gold diggings. From this reservoir, he conducts the water by enormous hose toward the region where the workings are to be conducted. When everything is ready, the valves are opened and a stream of water from the hose is directed against the earth and gravel in the neighborhood of the sluice. The earth is torn away by the tremendous force of the water. Whole hillsides may thus be washed into the sluice, and practically all the gold in them may thus be obtained.

The streams of water used were at first delivered from nozzles of an inch in diameter; little by little larger ones were employed until at last a nine-inch

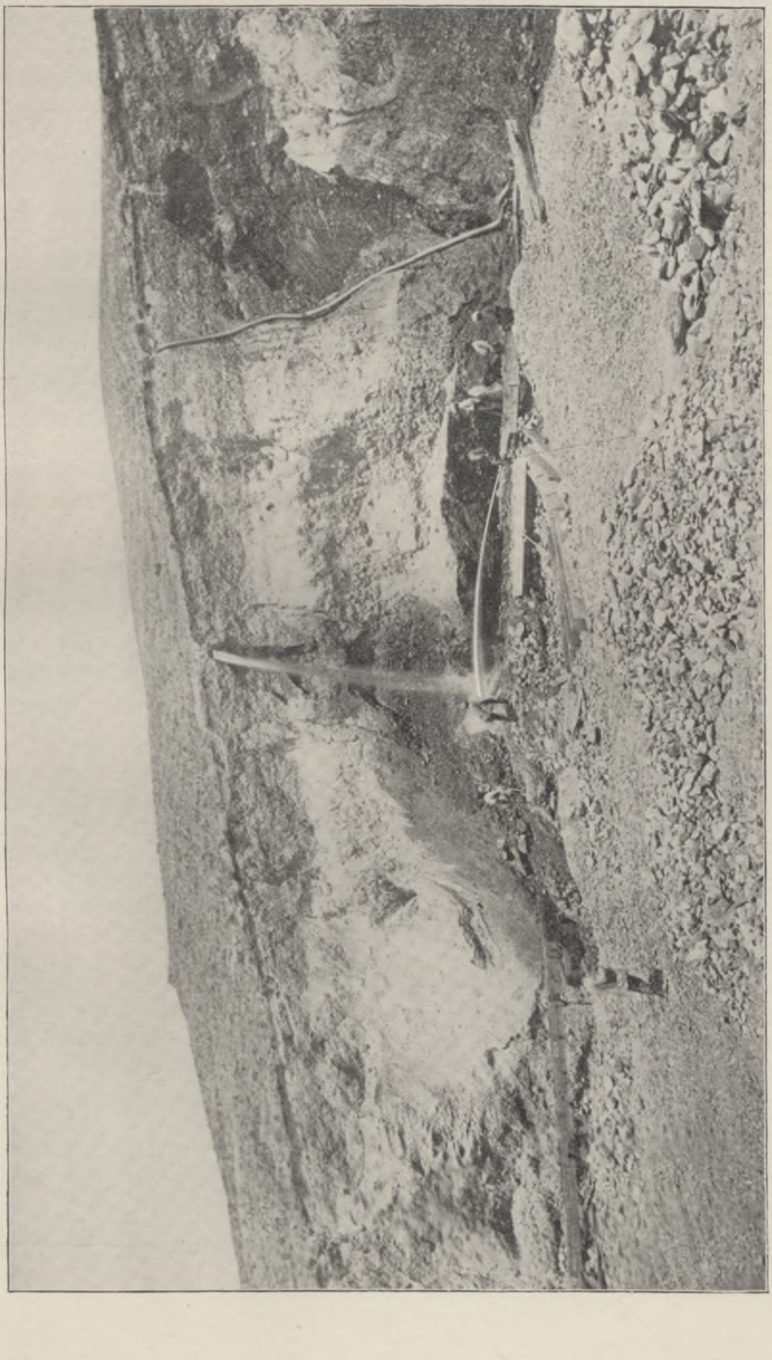

Fig. 47. Washing auriferous earth by the "hydraulic" method.

stream became common. Such a stream is capable of delivering 185,000 cubic feet of water an hour at a velocity of 150 feet per second.

In California, hydraulic mining was at one time carried to such an extent as to give rise to the most injurious results. Rivers became so filled with boulders and debris as to produce disastrous freshets and to flood large areas of adjacent territory. Many important farming sites were practically ruined. The bed of the Bear River was raised 97 feet in one place and 150 feet in another. On the Yuba river, farm lands to the extent of from fifteen to sixteen thousand acres were covered with detritus. In a certain case a farm on the Yuba river had, in 1857, banks twenty-two feet high at low water; in 1862 the same fields were flooded six feet deep; in 1878 they were buried under twenty-five feet of sand, reaching the tops of the telegraph poles. The owner had to dig five feet to reach the top of his garden fence. His house was flooded with water.

As the result of litigation upon this subject, the courts issued injunctions stopping such hydraulic mining.* The effect was to seriously reduce the output of gold for the State of California. In 1880, the gold product for this state was nearly eighteen million of dollars in value. In 1890, it was nearly ten millions. Subsequent laws have permitted resumption of the use of the method but subject to the application of remedies for the evils. Among such remedies are the construction of great retaining dams to hold back, near their source, the coarser earthy materials washed out of the soil by this method.

Dredging. — While the excavation of earth is done by hand in "rocking" and in "sluicing," it is accomplished by water-power in "hydraulicking." "Dredging," however, uses steam power. Where water is deficient dry dredging is employed; where water is abundant or even moderate in quantity, floating dredging is employed.

The floating dredge (delivered from a manufacturing establishment in parts) is transported to the mining regions; it is erected in the bed of a small stream. Then a rough dam is built on the stream *below* the dredge. The water is retained and it makes a small lake which floats the dredge. The scoop digs up the soil, delivers it to a sluice of steel on the dredge. In this sluice the gold is recovered and the tailings are delivered back of the dredge. Thus the dredge floats up stream, the artificial lake following it.

A traction dredge may work on a similar general principle but in a comparatively dry region. It may operate somewhat as a railroad steam shovel does. It may be advanced, from time to time, on a rude roadway of joists. The excavated earth is worked for gold on the dredge. The dredge opens its own road and works steadily forward through the auriferous deposit.†

The Milling Process.

This process involves as its basal principle a thorough crushing of hard ore in order to uncover the finest particles of gold present; this is preparatory to collecting the gold in metallic mer-

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* *Sci. Amer.*, July 18, 1891, p. 33.

† *Eng. & M. J.*, 64: 605, 755.

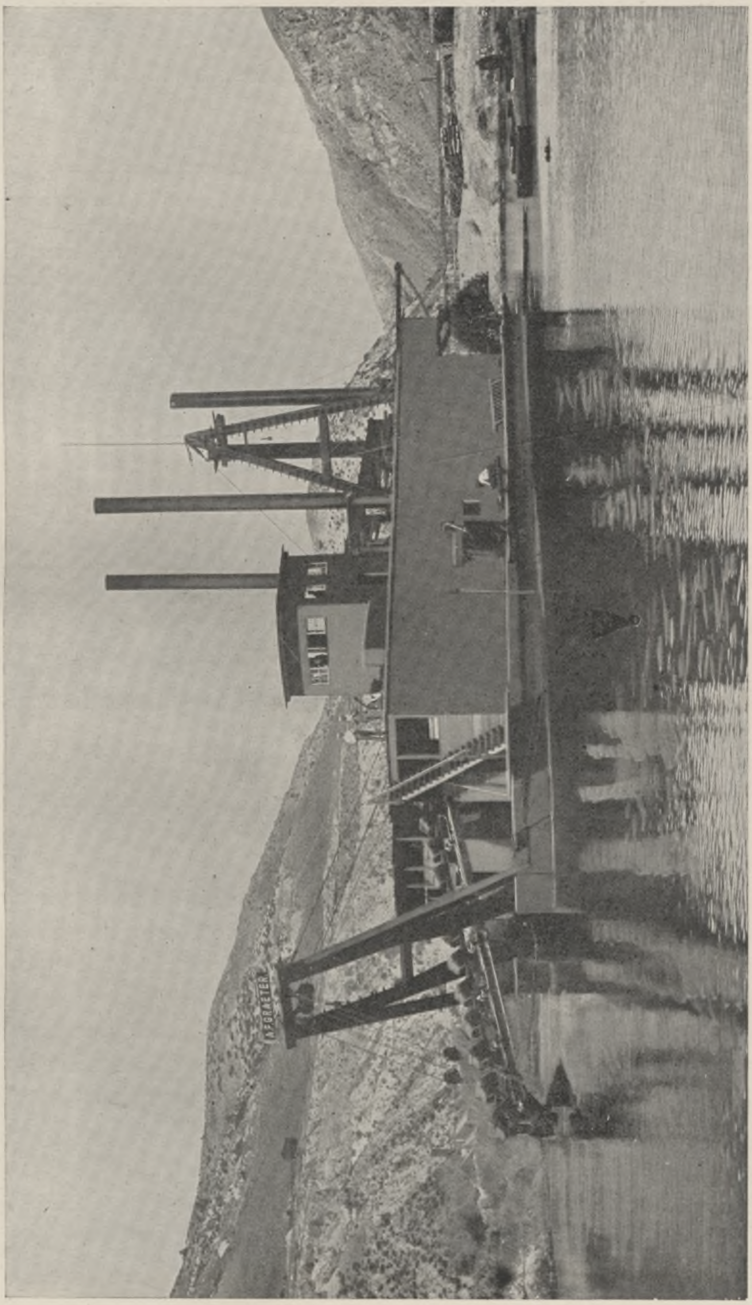

Fig. 48. Floating dredge for gold placer mining. (Built by the Bucyrus Co., So. Milwaukee, Wis.)

cury — "amalgamating" it. Taking the process in its completest development, although even then a simple one in theory, it stands as "the cheapest way of extracting gold devised by the ingenuity of man."

— The ore is broken in a stone-crusher.

— Next it goes to the stamp-mill. Here it is crushed to a very fine powder. The unit of the stamp-mill is a mortar and pestle, but many such are grouped together in a "battery." On the long "stem" of each pestle is a sleeve — the "tappet." On the power shaft is a series of cams. As the shaft revolves the cams raise the stamps; then they fall by gravity. The mortar is a strong iron casting; it is provided on one side with a sheet of perforated metal called the screen. As the mixture of ore and water in the mortar is struck by the pestle, the "pulp" splashes against the screen and the finer portions pass through to the amalgamating table. Sometimes the mortar is supplied with a little mercury; sometimes it is furnished with an amalgamated plate.

— The amalgamating tables are in a sense sluices. They often have riffle bars. They contain amalgamated copper plates. (Often these plates are silver-plated before the mercury is rubbed on.) Gold is caught by the mercury of the mortars and by the amalgamated plates. Subsequently this amalgam is strained and "retorted."

— The pulp from the amalgamating tables goes to the "vanner." The vanner is essentially an endless rubber belt moved by machinery in a direction opposite to the current of "pulp" and water. The belt receives a pulsating sidewise motion also. Thus the pulp is agitated slightly but regularly and determinately in the water. As a result the particles of heavier mineral — pyrites and the like — travel with the belt *upward* and against the current of water provided for them. (As they are auriferous they are subsequently roasted and chlorinated.)

But the particles of lighter rock travel *downward* with the water. Such particles make up the "tailings." (Since they contain extremely minute particles of "float" gold, tailings are often treated again — best perhaps by "cyaniding.")

Chlorination.

This process depends upon the fact that free chlorine dissolves metallic gold, forming a soluble compound. The chlorine is usually generated by the action of dilute sulphuric acid upon bleaching-powder.

The process is applicable to most ores of gold that do not carry much silver. It is largely applied to ores carrying auriferous pyrites and to the pyrites concentrated on the vanners after milling.

The process is carried out somewhat as follows:

If ore is used it is crushed and "concentrated." One hundred tons of ore may thus be reduced to nine tons of "concentrates."

The "concentrates" are carefully roasted. The roasted ore is transferred to lead-lined iron barrels. To these, water, bleaching-powder, and dilute sulphuric

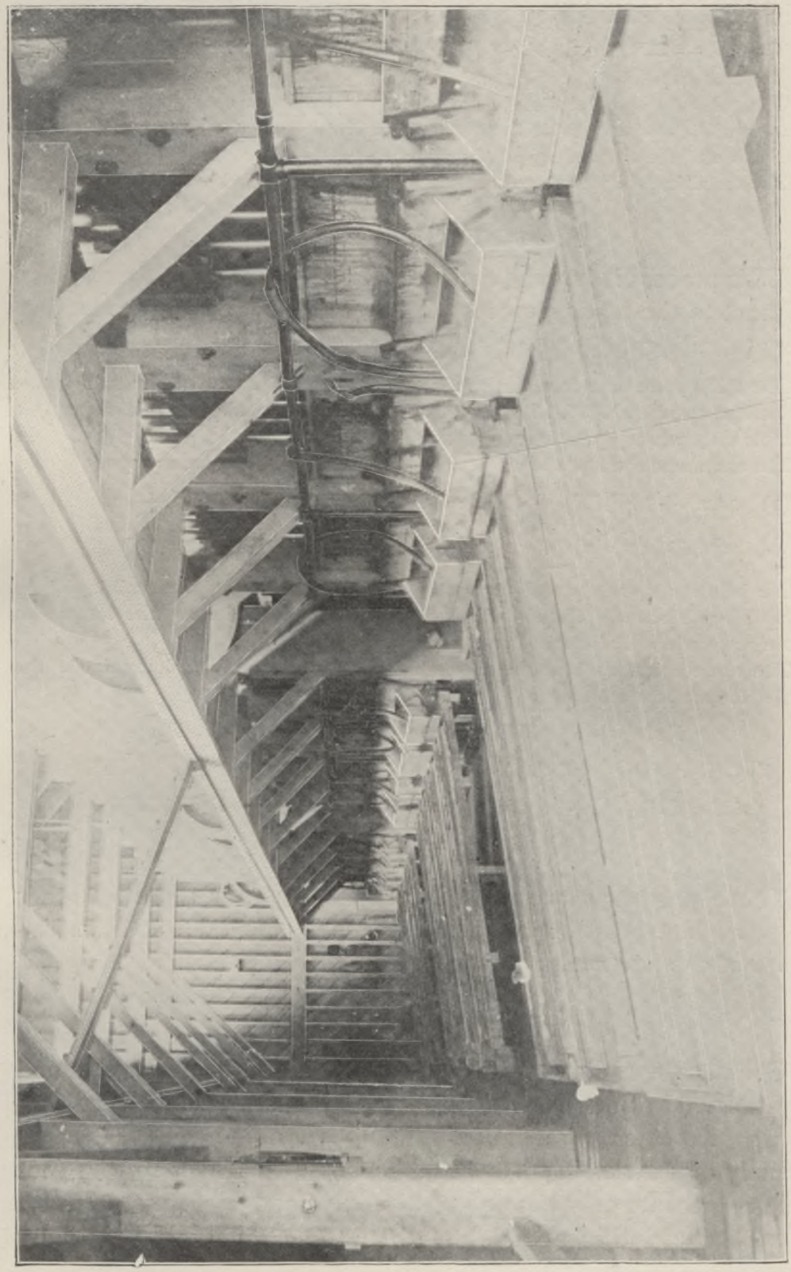

Fig. 49. Interior of a "stamp mill." The stamps are at the right. The amalgamating tables stretch from right to left.

acid, are added. The barrels are closed and agitated by machinery. Little by little the gold forms soluble auric chloride, $AuCl_3$.

When the gold has completely dissolved, the watery mass is filtered, the gold being in the liquid.

The gold may be precipitated as metallic gold by ferrous sulphate. Or it may be precipitated as a sulphide by sulphuretted hydrogen gas (after previous neutralization of the chlorine by sulphur dioxide gas).

The metallic gold (or the gold sulphide) is then dried and melted in a crucible.

Cyaniding.

This process is largely used in South Africa and there, as an adjunct to the milling process, it has been applied with great success to tailings.

The tailings are transferred to two large tanks containing a dilute solution of potassium cyanide, KCN. This solution dissolves the metallic gold forming a soluble salt, aurous potassium cyanide, $KAu(CN)_2$.

The exact reaction has not yet been determined; two forms are proposed:

(1) $2Au + 4KCN + H_2O + O = 2KAu(CN)_2 + 2KOH$

(2) $Au + 2KCN + H_2O = KAu(CN)_2 + KOH + H$

The solution is subsequently drawn into another set of tanks containing shavings of metallic zinc. The zinc displaces the gold, precipitating the latter as a metallic powder. It is melted and cast into bars.

The exact reactions brought about by the zinc are not yet determined; the probable reactions are these:

$$Zn + 2H_2O = ZnO_2H_2 + H_2$$

$$ZnO_2H_2 + 4K(CN) = K_2Zn(CN)_4 + 2KOH$$

$$2KAu(CN)_2 + Zn = 2Au + K_2Zn(CN)_4$$

Other Processes.

These processes are subordinate to those for securing other metals. The most important are those incidental to the metallurgy of copper (see p. 90) and of silver (see p. 93).

Properties of Gold.

Gold has a well-known yellow color. It is sometimes found crystallized in the earth in cubes or octahedrons. It is very ductile, so that it may be drawn out into very fine wire. It is extremely malleable. It has been beaten into leaves so thin that each represents only the one two hundred and eighty thousandth of an inch in thickness. The thinnest of gold leaf is actually translucent, allowing light to pass through it.

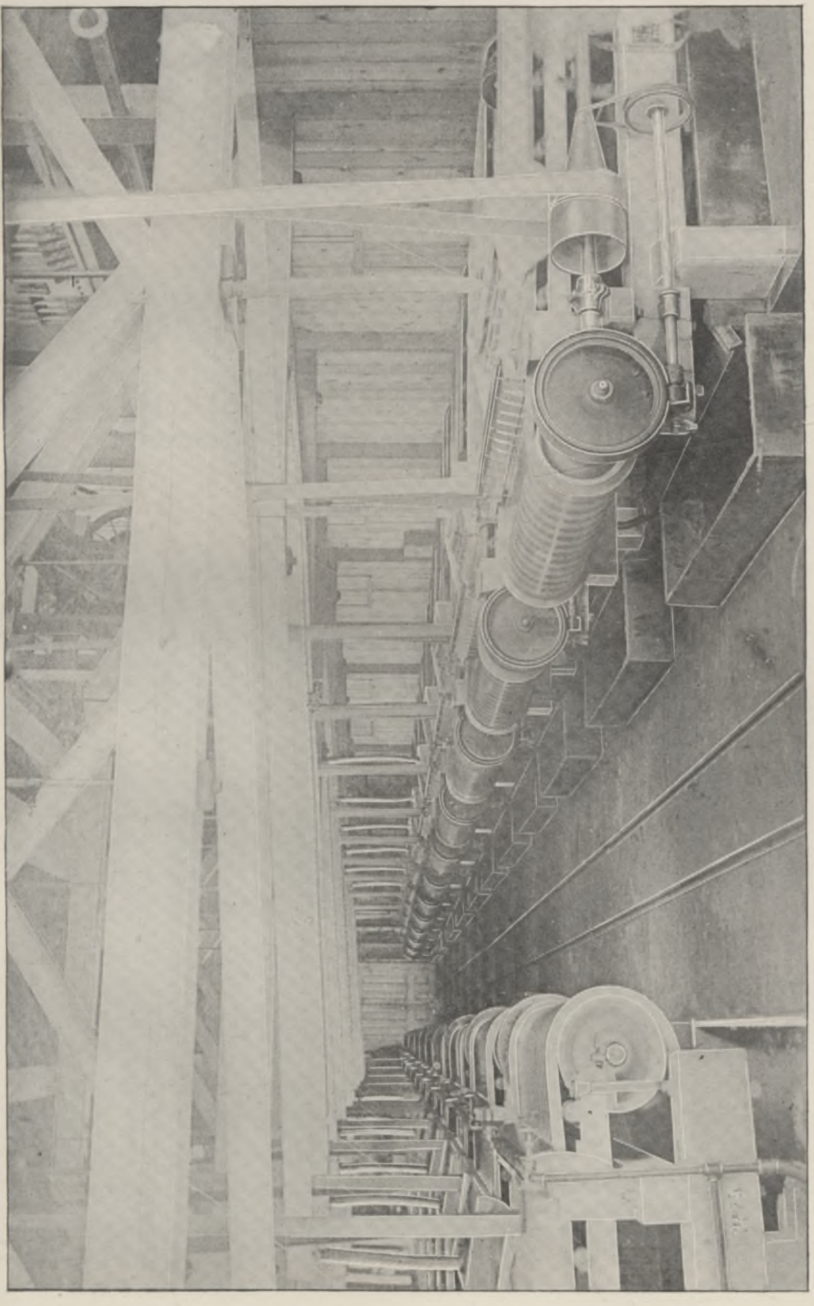

Fig. 50. "Vanners" for concentrating ore. (The other end of one of the machines is shown at p. 86.) Powdered ore and water are brought by hose from the room above, and deposited on the belt. The heavier and more valuable ore clings to the belt (it is removed in the boxes below); the lighter and comparatively worthless rock is washed away at the other end of the machine.

Chemically, gold is very inert: it manifests but slight tendency to unite with other elements, and even when compounds have been formed, they decompose very easily — liberating the metal. Many compounds of gold are known to chemists — but most of them are produced by what may be called indirect processes. Gold is not acted upon by ordinary acids; its appropriate solvent is a mixture of nitric acid and hydrochloric acid, called aqua regia, which dissolves it, producing either auric chloride, $AuCl_3$, or hydrochlorauric acid, $HAuCl_4$.

A Few Compounds of Gold.

With chlorine;	Aurous chloride,	$AuCl$;	Hydrochlorauric acid,	$HAuCl_4$
			Sodium hydrochloraurate,	$NaAuCl_4$
	Auro-auric ——	$AuCl \cdot AuCl_3$;	Potassium ——	$KAuCl_4$
	Auric ——	$AuCl_3$;	Ammonium ——	NH_4AuCl_4
With bromine;	Aurous bromide,	$AuBr$;	Hydrobromauric acid,	$HAuBr_4$
	Auro-auric ——	$AuBr \cdot AuBr_3$;	Potassium hydrobromaurate,	$KAuBr_4$
	Auric ——	$AuBr_3$		
With iodine;	Aurous iodide,	AuI		
	Auric ——	AuI_3;	Potassium hydroiodaurate,	$KAuI_4$
With oxygen;	Aurous oxide,	Au_2O		
	Auro-auric ——	AuO;	Aurylic hydroxide,	$AuO \cdot OH$
	Auric ——	Au_2O_3;	Auric ——	AuO_3H_3
With sulphur;	Aurous sulphide,	Au_2S;	Sodium aurosulphide,	$NaAuS$
	Auro-auric ——	AuS;	Auric sulphate,	$AuSO_4$
With nitrogen;			Auric nitrate,	$Au(NO_3)_3$
With phosphorus;	Auric phosphide,	Au_2P_3		

Auric chloride, $AuCl_3$, is obtained by dissolving pure gold in aqua regia and then carefully evaporating the solution to dryness. When heated, the compound decomposes, chlorine is liberated, and aurous chloride, $AuCl$, is produced.

Auric chloride manifests a strong tendency to form double salts with hydrochloric acid and soluble metallic chlorides. With hydrochloric acid, the result is hydrochlorauric acid, $HAuCl_4$; with metallic salts, double compounds of similar type are formed.

Auric oxide, Au_2O_3, may be prepared from auric chloride by the addition of magnesium oxide. A brown precipitate is produced. Auric oxide is easily decomposed into gold and oxygen. It unites with water to form a hydrate, H_3O_3Au. This substance is sometimes called auric acid, because of its tendency to unite with the metals to form a series of salts.

Aurous cyanide, $Au(CN)$, is known. It may be formed when metallic gold is dissolved in a dilute solution of potassium cyanide. It tends to form double cyanides like aurous potassium cyanide, $AuCN{\cdot}KCN$.

Auric cyanide does not appear to exist alone, but it exists in many double cyanides like auric potassium cyanide, $KAu(CN)_4$. This latter salt corresponds chemically with hydrochlorauric acid already referred to. It is easily soluble in water and is much used in the electro-deposition of gold.

Purple of Cassius is a dark colored compound varying in hue according to its method of preparation. While its exact molecular composition has not been satisfactorily made out, it is known to contain gold, tin, and oxygen. It is best prepared by employing a solution containing tin in both the stannous and stannic forms.

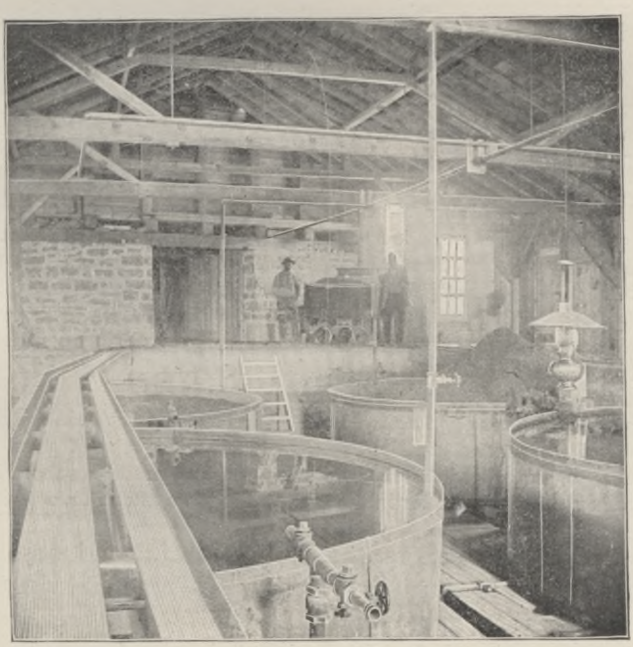

Fig. 51. Cyaniding. The tanks contain ore, and solution of potassium yanide to dissolve out the gold.

To this, a dilute solution of auric chloride may be added. Purple of Cassius is used as a pigment on porcelain and glass. When the article is fired, a beautiful red color is produced where the purple of Cassius was applied.

Uses of Gold and its Alloys.

Pure gold is rarely used — an alloy of gold with copper or silver or both at once, while maintaining the yellow color of the pure metal is harder as respects wear, and of course cheaper.

The proportion of gold in an alloy is expressed in *thousandths* or in "carats." The word carat properly means one twenty-fourth. Thus, pure gold, technically termed *fine gold,* is said to be twenty-four carats fine. Similarly, an alloy containing one-half gold is said to be twelve carats fine. In some parts of Europe, the standard adopted for the best jewelry is eighteen carats. An alloy that is harder and better fitted for wear is of fifteen carats.

Among the chief uses of gold and its alloys among enlightened nations are the following:

First, it is used in the manufacture of coins and as a standard of coinage. A distinction should be made between these two uses. In some of the great nations of the world at the present day, it is preserved in the form of *gold bars* as a basis for a paper circulating medium.

The gold coins of the United States, of France, of Germany, and of some other nations, are nine hundred one-thousandths fine. The gold coins of Great Britain (made from a twenty-two carat alloy) contain nine hundred and sixteen and sixty-six hundredths parts of gold per thousand parts of coin.

English mint officials have estimated that the "life" of the coin called the sovereign is only nineteen years, and that of the half sovereign only nine years. The wear, therefore, of gold coin is so considerable that of late various attempts have been made to avoid the serious loss and inconvenience occasioned by it. On the one hand, it has been proposed to issue paper notes to replace a portion at least of the gold in actual circulation. On the other hand, a royal proclamation of Nov. 22, 1890, announced that all gold coins of reigns preceding that of Victoria would cease to be legal tender in the United Kingdom after Feb. 28, 1891.

Second, it is employed in the various useful and ornamental articles known in general as jewelry. Thus a gold watch case represents a portion of a useful article and is not a mere ornament.

Third, in the form of gold leaf and in the form of electro-deposited gold, it is largely employed for various useful purposes where beauty is at the same time desired. Thus, large quantities of gold leaf are employed in book lettering, sign painting, on picture frames, and on various small objects of inferior metal.

There are three principal methods of gilding. The *first* consists essentially in gluing thin gold leaf to some surface. The adhesive material commonly used is called "size." It is a highly tenacious gum produced from linseed oil. A *second* method is that called fire gilding. In this, an amalgam of gold (an alloy of gold and mercury) is first spread upon the surface of the metal to be gilded, and subsequently, the coated material being heated, the mercury is volatilized and the gold remains as a thin layer. The *third* method is that of electro-deposition The object to be coated is properly prepared, then attached to the negative electrode of a battery, then immersed in the solution of gold. Upon allowing the electric current to flow through the solution, a film of gold is deposited upon the object.

Several important *mechanical* methods have been devised for producing upon wire a thin coat of gold. They are in principle somewhat like the following: A short tube of gold is filled with some inferior metal, or alloy. A thick short rod is thus produced. This composite rod is next drawn through some form of wire-drawing machine, until it produces a long and fine wire completely coated with a thin shell of gold. Such wire is now largely employed in the manufacture of rings, watch chains, and other objects of jewelry.

Fourth, considerable quantities of gold are consumed in some of the operations of photography.

Fifth, gold is used to some extent in imparting to glass and porcelain a ruby color. Such glass is of course expensive.

Appendix. — The Chief Gold-producing Districts of the World.

The chief sources of gold for the ancient world were northern Africa, India, and certain parts of Siberia. The ancient Romans appear to have obtained gold from some parts of Spain. The sands of the Rhine have been worked, for the moderate quantities of gold contained in them, for more than a thousand years. The precious metal appears to be derived from the pulverized rocks of the Alps, the powder being carried, little by little, into the streams originating in these mountains.

At the present time gold is produced from the territory of every continent, and from several different geographical divisions of those continents; but more than three-fourths of the world's annual supply is furnished from four countries: the United States, the South African Republic, Australasia (Australia and adjacent islands), Russia.[*]

It is difficult to determine very closely the total output of gold from the earth. Several statisticians give annual estimates, but owing to the circumstances of the case these estimates vary somewhat. In the following table is presented in round numbers the

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[*] U. S. Mint, Director of. — *Annual Reports.* Washington, D. C.

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Brown, A. S. and Brown, G. G. — *The Guide to So. Africa.* London, Sampson, Low, Marston & Co.

— The files of the *Eng. and Mining Jour.* (N. Y.) contain a vast amount of scientific information on mining and metallurgical subjects.

— The *Indexes to Periodical Literature.* (Poole's Index, the Cumulative Indexes, and others) refer to many articles on gold and gold mining — some of them scientific, some of them popular.

— In Charles Reade's *Never Too Late to Mend*, is a romantic treatment of the story of the discovery and working of gold in the early days of Australian exploitation.

world's production of gold for a series of years, and also the contributions of the four chief producers :

Annual Output of Gold. (Round numbers in *millions of dollars* of value.)

	World.	U. S. A.	S. African Rep.	Australasia.	Russia.	Others.
1887	105+	33+	.7+	26+	20+	Not given here.
1888	110+	33+	3+	26+	21+	“ “
1889	120+	32+	7+	31+	23+	“ “
1890	120+	32+	9+	29+	25+	“ “
1891	122+	33+	14+	31+	24+	“ “
1892	141+	33+	22+	33+	24+	“ “
1893	158+	39+	28+	34+	28+	“ “
1894	182+	39+	38+	39+	26+	“ “
1895	201+	46+	42+	42+	31+	“ “
1896	212+	52+	41+	43+	31+	“ “
1897	238+	59+	56+	53+	29+	“ “

Other studies of this subject indicate that the world's total output of gold increased with more or less steadiness — though from time to time with very large strides, — from the period of the discovery of the New World down to 1880. From 1880 to about 1884, there seems to have been a distinct falling off in production. Commencing with 1884, the production has increased steadily. The increase in recent years too has been very marked. This increase is partly referable to the growth in the demand for gold by the governments of great nations. In response to this demand, improved scientific methods of securing the metal have been invented and employed. Again, more active search has been promoted; it has been rewarded by the discovery of new sources, notably in certain sections of the United States, in British Columbia (the Yukon District), and in South Africa (in the South African Republic, the so-called Transvaal).

Early methods of gold mining were applicable only to ores at once rich and easily loosened by water. The miner often worked with little experience, his expenditure of labor was extravagant, and he was obliged to lose a considerable percentage of the gold really present in the earth worked. At the present time gold mining is generally conducted as a stable business enterprise, like the mining of coal or of iron.

The territory to be worked is examined by skilled geologists. The approximate amount of gold contained in the territory is determined by excellent appliances, such as diamond drills. The ore is gotten out, even when the deposits are from hard quartz rock, by the use of the best mining appliances. The mills for working the ore are constructed with reference to the highest economy of operation, and they are controlled by superintendents of large experience and often of thorough scientific training.

As a result, in a given mine and mill, all the ore that will pay is worked, none is lost sight of; again the tailings are continually assayed so that the loss in them may be as little as possible. Fuel is used economically. In some cases the machinery is operated by water-power; the energy being conducted by means of electrical wires from the water-falls to the mills. The mine may be even lighted by electricity from the same source. Electricity may also be employed for producing decomposition of common salt for the chlorination department; or again it may be employed for precipitating silver and gold, as in the electrolytic precipitation of auriferous and argentiferous copper.

Gold in North America.

The early navigators who reached the Western Continent, had great hopes of obtaining gold there; and considerable quantities of the precious metal were collected in South America and in Mexico.

In the early history of the United States, gold was found in North Carolina, Virginia and Georgia; and mining has been carried on in these states even to the present day.

Fig. 52. Sluice of Sutter's saw-mill in the Coloma valley, California, where Marshall made the discovery of gold.

Fig. 53. Northern Light mill, near Ophir, Utah. (The uplifted beds of the Mercur district show on the mountain in the back-ground.)

In the year 1848, gold was discovered in California. This find has proved one of the most momentous occurrences in the commercial history of the world.

In 1839 John A. Sutter, "a Swiss by parentage, a German by his birth in Baden, an American and later a Mexican by residence and naturalization," settled in California at the junction of the Sacramento and American rivers, near the site of the present city of Sacramento. He built a rude fort there. In 1848 he commenced to build a saw-mill in the valley of Coloma, in the mountains, about forty-five miles from the "fort." James W. Marshall of New Jersey selected the special site and he superintended the construction of the mill.

One morning (Jan. 24, 1848) Marshall while inspecting the mill trench picked out a piece of yellow metal in the sands. For a few weeks little was thought of it, but the news soon spread to San Francisco, and after some early visitors had been very successful, the news extended all over the world. An unparalleled tide of emigration was started. Americans, Europeans, even Asiatics, flocked to California.

For a great many years California was the chief source of gold of the United States, and one of the most productive regions of the world. But by reason of legal interference with *hydraulic mining*, California suffered for a while a diminution of output.

The discovery of gold in Colorado, made in 1858, gave rise to active operations there. For a while the gold output of Colorado was of less value than its silver output, but within a few years, owing to increased demand for gold, and improved metallurgical methods, Colorado has taken its place at the head of gold-producing districts in North America.

The following table presents a statement in round numbers of the value of gold produced in the several important districts of the United States:

Output of Gold of the United States for Year 1897.
(In round numbers.)

Colorado	19+	*million dollars*
California	15+	"
South Dakota	5+	"
Montana	4+	"
Nevada	3+	"
Alaska	2+	"
Arizona	2+	"
Idaho	2+	"
Utah	1+	"
Oregon	1+	"
Others	4+	"
Total, United States, for year 1897	59+	"

The lowest output of gold by the United States in recent years was reached in the period from 1881 to 1885. Since the latter date there has been a steady, and in some years a very large increase.

At about the time of the discovery of gold in California, this metal was also observed in Alaska. Comparatively little attention was paid to it, however, because the region was so remote and inhospitable. Of late, however, considerable mining has been carried on in a systematic manner; but the resources of the Alaskan mines are by no means at present fully known, much less developed.

In the southern extremity of Alaska, near Juneau, are important auriferous quartz deposits, although the amount of gold in the rock is proportionally small, yet the conditions prevailing have proved highly favorable. The deposit is extensive, and it is worked by large and carefully conducted companies. That called the Alaska-Treadwell Co. is said to operate the largest stamp-mill in the

Fig. 54. In the pit — Alaska-Treadwell mine, near Juneau, Alaska. The men are drilling the rock preparatory to blasting.

world. The deposit is near tide water, so that no difficulty is experienced in getting rid of waste rock.

The workings near Juneau must be distinctly discriminated from those in the Yukon District, 750 miles farther north.

In 1896 returning miners from the Yukon District brought reports of very rich placer deposits of native gold near the Klondike River, in British Columbia. The gold brought back, and the stories distributed, produced great excitement As yet there is not sufficient trustworthy information on which to base an opinion as to the future of this district. It is plain that it contains important deposits of free gold, but the conditions are in many ways very unfavorable. Lack of easy communication and transportation to a region so remote from centres of civilization, and difficulties incident to the subarctic climate, most seriously interfere with productiveness.

Gold in South Africa.

The great and important gold fields of South Africa are at present those of the Boer free state, often spoken of as the Transvaal, but legally called the South African Republic. They are underneath the surface of a high plateau, called Wittewatersrandt, or "The Rand," not far from the city of Johannesburg (about 22° S., 29° E.)

As early as 1845, indications of gold were reported from South Africa: again in 1854 gold was discovered near the present site of Johannesburg, but the Boers, who preferred to lead a pastoral life, objected to mining operations. Notwithstanding this drawback, discovery followed on discovery, and at length a five-stamp battery was set up on the Wittewatersrandt in 1884. A good deal of excitement followed, reaching its height in the period from 1887 to 1889 — not only in the South African Republic, but also on the bourses of London, Paris, and Berlin, where South African mining stocks, called "Kaffirs," were dealt in on greatly inflated values.

The first important statistical record of gold from South Africa was for the year 1887. Since then the output has increased by rapid strides as is shown by the table already presented. (Page 131.)

The South African fields are worked under the direction of the highest engineering and metallurgical skill, and they have the advantage of native labor that

Fig. 55. Group of engineers, prospectors, and native laborers in the gold fields of South Africa. (The white men in the foreground are testing a sample of ore.)

Fig. 56. Washing auriferous earth by the hydraulic method (South Africa).

is low priced, though distinctly ineffective. They suffer from certain disadavantages, such as statutory limitations, and the relative scarcity of wood and water.

In the Wittewatersrandt, while many of the important workings are carried on near the suface, borings have shown that the gold-bearing rocks continue at least 2,400 feet. Placer methods are sometimes employed, and hydraulic mining is somewhat used.

But the ore, which is a firmly cemented conglomerate, is generally crushed and milled by the California method, and largely under the supervision of American engineers. The pulp running from the mills is concentrated by vanners. The concentrates are chlorinated. Then the tailings are cyanided; the cyanide process having reached a more successful development in South Africa than elsewhere. Milling secures 50 — 60 % of the assay value of the ore; chlorination of concentrates and cyaniding of tailings each yield 10 — 12 % more; showing therefore a total loss of precious metal of only 10 — 20 %.

It is believed that the mines will be lasting producers. Indeed, in the opinion of some observers, the African deposits will prove richer than any others now known.

Gold in Australasia.

The term Australasia is intended to include the several districts of the great continental island, Australia: Victoria, Queensland, New South Wales, Western Australia, South Australia (none reported from North Australia), and also the adjacent islands — Tasmania and New Zealand.

In 1841 Mr. Clarke, a colonial geologist, affirmed that gold exists in Australia; in 1844 Sir Roderick Murchison announced that the geological formations indicated the probability of gold deposits, and he advised search for them.

There is reason to believe that the existence of gold was known several years earlier, but the information was suppressed under the fear that, since the territory was the seat of a penal colony, a knowledge of the presence of gold might make government more difficult, and moreover would be disadvantageous to the agricultural interests!

On the 3d of April, 1851, Edward Hargraves, a Californian miner, informed the Government that he had discovered valuable deposits of gold and he proceeded to prove his statement by showing the official geologist the place at Summerhill creek near the town of Bathurst, 150 miles from Sydney, New South Wales. About six weeks later gold was discovered in the colony of Victoria at Ballarat near Melbourne. The result was an enormous immigration with excitement similar to that produced by the discoveries in California.

Australasia has since furnished an immense amount of the precious metal, so that, as one of the tables shows, it has become one of the first of producers. A few of the Australasian mines have diminished output in recent years, but others have increased, notably those of Western Australia (sometimes called Westralia). The general total has increased, however.

Gold in Russia.

The gold referred to as produced in Russia is largely the result of convict labor applied with inferior apparatus and machinery. Under such conditions the output must be unsatisfactory. It is believed, moreover, that notable amounts of the metal are lost by theft. Again, it is thought that the statistics are unworthy of the highest confidence.

General Remarks.

— In many cases where subjects relating to gold (and indeed to other metals) are considered it is necessary to make a careful distinction between the *cost*, the *selling price*, and the *value* of the metal.

The *cost* of gold is measured by the amount of effort expended in obtaining it from the earth — in long search for its ores, and in hard labor in getting out a given weight of metal.

The *selling price* is measured by the labor or services, the materials or desirable things, that must be offered to the possessor of gold in order to persuade him to part with a given weight of the metal.

The *value* depends upon the utility of the metal when it is obtained; and this utility is based upon its special and exceptional physical and chemical properties. Thus the utility of gold in a coin is due to its incorruptibility, to the fact that it does not decay, oxidize, corrode, or otherwise suffer any considerable depreciation in mass during a long period of preservation. Its utility in the arts is referable to much the same set of physical and chemical qualities. Thus, gold lettering on books retains its color and brilliancy.

— It is recognized that, while in the early days of California and Australia some of the miners secured large profits, many of them secured none. It is estimated that in the best days of Californian mining, the average pay of the miner was little over one dollar per diem — and this under conditions where cost of living and supplies was very high. It has even been stated that the cost of labor and supplies for the production of the gold and silver of the world has been greater than the price brought by these metals in the market.

"In well-established and economically managed mines and mills the actual cost of mining, crushing, amalgamating, retorting, etc., in a free-gold mill, may be taken as at a minimum at the Deadwood-Terra mine in South Dakota; here the cost is about $1.25 per ton of ore, 500 tons a day being crushed by 160 stamps.

At the Alaska-Treadwell Company's works the average total cost [in 1892] was about $1.50 per ton, on a very large output. Where veins are smaller and output less, the cost increases. . . . . .

The necessity for extra handling, etc., due to irregularities in the ore bodies, changes in the character of the ore itself, etc., etc., may bring costs up to $10 per ton. In some large mines, the cost varies from $1.50 up to very high figures, and may be roughly averaged, at present, as about $20 per ton." *

— A question like the following is frequently asked: What is the average content in valuable metal, of the ore of a certain mine? Before such a question can be answered it is essential that the term "ore" be freed from ambiguity.

1st — Suppose that the company owns a square mile of land and that it is capable of driving a shaft a mile in depth; a cubic mile of earth is here involved. *It is not ordinarily practicable nor necessary to estimate the average percentage of valuable metal* in this cubic mile of earth.

2d — Suppose the property is penetrated by veins of ore. *Assays of portions of the prevailing ore in the veins give useful information but are often highly misleading.*

3d — Suppose that the shafts are sunk and the mineral is being excavated. It is highly desirable to make *assays of the ore brought to the surface*; *an average of a large number of such assays of thoroughly representative samples*, affords a basis for a statement of the amount of the valuable metal existing in the ore worked.

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* *The Mineral Industry*, I, 224.

BOOK II. — SECOND PERIODIC GROUP.

1st Section. — CALCIUM, STRONTIUM, BARIUM.

2d Section. — BERYLLIUM (GLUCINUM), MAGNESIUM, ZINC, CADMIUM, MERCURY.

General Comments on Calcium, Strontium, and Barium.

Calcium, strontium, and barium are metals, but they are never found in nature in the metallic form. Further, they are never used as metals in the arts. They are chemical curiosities that may be prepared by suitable specially devised processes.

When either one of them is produced artificially, it is observed to have such active affinities, that, if exposed to the air, it readily absorbs atmospheric oxygen and combines with it. By this combination, the metal ceases to remain a metal — it becomes an oxide.

In the earth these three metals exist in the form of compounds which appear as mineral masses.

So far as man is acquainted with the composition of the terrestrial globe, it appears to contain these elements in very different quantity. Thus, compounds of calcium are extremely abundant, and they are widely diffused, so that this element may be classed as fifth or sixth in order of abundance, but compounds of barium and strontium are recognized in the earth in very much smaller proportion. It may be added incidentally that in correspondence with their preponderating abundance, calcium compounds are employed by man in vastly greater quantities than barium compounds, or strontium compounds. Possibly also this relatively larger employment of the calcium compounds may be referable to a somewhat ampler range of chemical properties.

Calcium, strontium, and barium form compounds that are characterized by marked resemblances, both in qualities and in molecular structure. The majority of the compounds of these metals are colorless. Although this may appear to be a superficial characteristic, it is indeed a significant one, and one that points to fundamental resemblances between the substances under discussion.

The metals in question form similar oxides :

Calcium oxide, called either lime, or quicklime	CaO
Strontium oxide, sometimes called strontia.	SrO
Barium oxide, sometimes called baryta.	BaO

The formulas of these oxides show them to be of similar type of chemical structure. Moreover, they possess decidedly similar properties ; thus they are often spoken of as *alkaline earths* and the term conveys in brief, a statement of their principal characteristics.

The corresponding sulphates have resemblances :

Calcium sulphate	$CaSO_4$
Strontium sulphate	$SrSO_4$
Barium sulphate	$BaSO_4$

These three salts are white in color and when artificially prepared are powdery in form. None of them are very soluble in water, one of them, i. e., barium sulphate, being one of the most insoluble salts known.

Again, the three carbonates are similar :

Calcium carbonate	$CaCC_3$
Strontium carbonate	$SrCO_3$
Barium carbonate	$BaCO_3$

These carbonates are also white and neither of them dissolves readily in water, but all of them dissolve readily in certain acids, for example, in hydrochloric acid and in nitric acid.

The metals of the Second section possess certain resemblances, but they are of a less striking form than the foregoing.

CALCIUM; Ca; 39, 99.

Introduction — Distribution, preparation, and properties of calcium — Calcium compounds, especially the chloride, the oxide (quicklime), the sulphate, the carbide.

Appendix — Bleaching-powder.

Data for Reference.

Density of solid calcium, 1.57 (water being the standard = 1).
Fusing point of solid calcium, at red heat.
Boiling point of liquid calcium, above 950° C.
Calcium, as a new metal, was discovered by Sir Humphry Davy in 1808.
The name calcium is derived from the Latin word *calx*, meaning lime.

Introduction.

Calcium compounds have already been spoken of as existing among natural minerals in comparative abundance.

The early and wide use of mortars containing lime is certainly partly referable to the great abundance of the compounds of the latter substance in the earth.

As far back as the first century of our era, the preparation of quicklime from certain of its minerals was described by Dioscorides and Pliny. They clearly state that certain shells as well as limestone and marble, when strongly heated, give rise to a substance possessing characteristics very different from those of the original material whence it came. Further, they describe the great heat it evolves upon combination with water, its alkaline or caustic properties and its property of becoming mild, as distinguished from caustic, upon exposure to the air. From that early period, the study of calcareous minerals, such as limestone, marble, gypsum, and others, has continued with but little interruption.

The phlogistic chemists (who occupy a chronological position midway between that of the alchemists, and the chemists of the last hundred years) studied the phenomena of combustion. They gave careful consideration to the properties of quicklime as a peculiar heat-producing substance. They seem to have secured the important but not perfectly grasped idea that the heat of the burning fuel becomes somehow stored up in the quicklime, and that it is this heat that is re-liberated by the addition of water.

Toward the close of the eighteenth century Dr. Joseph Black of Scotland carefully investigated the phenomena referred to and he offered to the world clear and adequate chemical explanations of them as now accepted.

Distribution and Preparation of Calcium.

Most of the ordinary forms of earth which make up the soil of the globe, contain large quantities of calcium.

Again it exists in abundance in limestone. Now limestones are composed largely of calcium carbonate, $CaCO_3$. But limestone, in a form more or less pure, constitutes whole mountain chains.

Calcium sulphate occurs in nature in the form called gypsum, $CaSO_4 \cdot 2H_2O$, and in the form called anhydrite, $CaSO_4$.

Many other natural minerals contain calcium.

Calcium may be prepared by electrolysis of certain of its compounds, e. g., fused calcium chloride.

Properties of Calcium.

Calcium is a yellowish-white lustrous metal.

It oxidizes on the surface in ordinary, slightly moist, air.

It readily decomposes water at ordinary temperatures, forming calcium hydroxide.

A Few Compounds of Calcium.

With hydrogen;	Calcium hydride,	CaH_2		
With fluorine;	Calcium fluoride,	CaF_2		
With chlorine;	——— chloride,	$CaCl_2$;	Calcium chlorate,	$Ca(ClO_3)_2$
With bromine;	——— bromide,	$CaBr_2$		
With iodine;	——— iodide,	CaI_2		
With oxygen;	Calcium monoxide,	CaO;	Calcium hydroxide,	CaO_2H_2
	——— dioxide,	CaO_2;		
With sulphur;	Calcium monosulphide,	CaS;	Calcium hydrosulphide,	CaS_2H_2
	——— disulphide,	CaS_2		
	(——— polysulphides, in solution);	CaS_4; CaS_5;	Calcium sulphite,	$CaSO_3$
			Calcium sulphate,	$CaSO_4$
			——— potassium sulphate,	$CaSO_4 \cdot K_2SO_4$
			——— sodium sulphate,	$CaSO_4 \cdot Na_2SO_4$
			——— thiosulphate,	$CaSO_3S$

With nitrogen;		Calcium nitrate, $Ca(NO_3)_2$
With phosphorus;		Calcium hypophosphite, $Ca(PO_2H_2)_2$ Calcium orthophosphate, $Ca_3(PO_4)_2$ —— hydrogen phosphate, $HCaPO_4$ —— tetrahydrogen —— $H_4Ca(PO_4)_2$
With arsenic;		Calcium arsenites, $\begin{cases} Ca_3(AsO_3)_2 \\ Ca(AsO_2)_2 \\ Ca_2As_2O_5 \end{cases}$ Calcium arsenates, $\begin{cases} Ca_3(AsO_4)_2 \\ HCaAsO_4 \end{cases}$
With carbon;	Calcium carbide, CaC_2;	Calcium carbonate, $CaCO_3$
With silicon;		Many silicates

Calcium hydride, CaH_2. — Professor Henri Moissan who has prepared many new compounds with metals has produced calcium hydride by heating metallic calcium in an atmosphere of hydrogen under pressure.

The compound is white. When this hydride is brought into contact with water, both substances decompose, calcium oxide and hydroxide are formed, and hydrogen gas is liberated.

Calcium fluoride, CaF_2. — This compound occurs somewhat abundantly in nature as a mineral called fluor-spar.

Calcium chloride, $CaCl_2$. — This compound is easily produced by a variety of processes; the simplest is that in which quicklime and hydrochloric acid are mixed in appropriate quantities.

The salt has a powerful attraction for water: a dry mass of it exposed in an open vessel soon becomes liquid by absorption of water from the atmospheric air.

Solid calcium chloride is considerably used to absorb water from moist gases.

Calcium oxide, CaO. — This substance is readily produced by heating limestone, or marble, or some other form of calcium carbonate, $CaCO_3$, in a properly constructed furnace called a kiln. The limestone undergoes a loss of weight and a remarkable change of properties. It becomes quicklime, a substance having the formula CaO.

The chemical change is a very simple one:

$CaCO_2$ heated	=	CaO	+	CO_2
One molecule of calcium carbonate, 100 parts by weight.		One molecule of calcium oxide, 56 parts by weight.		One molecule of carbon dioxide, 44 parts by weight.
100			100	

The manufacture of quicklime is a most important industry. Indeed it has long been conducted in greater or less extent by civilized and even half-civilized peoples all over the world, on account of the wide use of the substance in mortars and cements.

The kilns in which the limestone is burned, are often so constructed that the carbonate and fuel (coke) may be introduced at the top, carbon dioxide may be conveyed away through a pipe for appropriate use, quicklime may be withdrawn from time to time for use of its kind; the working of the kiln may be continuous.

One of the most marked properties of quicklime is its lively action with water. When a piece of cold quicklime is placed

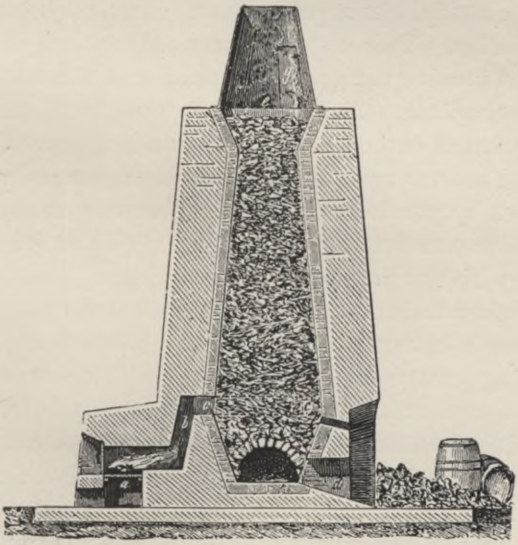

Fig. 57. Calcium carbonate (limestone) burned, decomposes. Quicklime remains, while carbon dioxide escapes.

in water, the water chemically combines with the lime in accordance with the following equation :

$$\underbrace{\underset{\substack{\text{One molecule of}\\ \text{calcium oxide,}\\ 56\\ \text{parts by weight.}}}{CaO} + \underset{\substack{\text{One molecule of}\\ \text{water,}\\ 18\\ \text{parts by weight.}}}{H_2O}}_{74} = \underbrace{\underset{\substack{\text{One molecule of}\\ \text{calcium hydroxide,}\\ 74\\ \text{parts by weight.}}}{CaO_2H_2}}_{74}$$

The change just mentioned involves true chemical union, and in common with most other chemical unions is attended with the evolution of heat and the production of a new substance with properties of its own. The heat of this union is so intense that ships transporting quick-lime are sometimes set on fire when, by accident, water reaches the cargo.

1 — As already intimated, the chief use of quick-lime is in the preparation of mortar and cement. In these cases, the lime having been slaked with water, is mixed with sand in the proportion of one part of lime to three of sand. When the mixture is put into use, it slowly undergoes a chemical change which manifests itself very quickly, but requires years, even centuries, for its absolute completion. This change, commonly spoken of as "drying," does indeed involve the gradual expulsion of the water which combines with the lime. The expulsion is accomplished largely by the absorption of carbon dioxide. Thus it appears that, curiously enough, the mortar comes to be bound together by calcium carbonate, i. e., by precisely the same substance started with, when the limestone was first heated for lime. (The sand also combines somewhat with the lime to produce silicate of lime.)

2 — Another and most important avenue for the consumption of quicklime is in connection with the modern or chemical method of bleaching cotton and linen goods. The recent enormous growth of the manufacture of cotton cloth has led to the gradual increase of the production of *bleached* goods. Ordinarily, one of the first steps in bleaching is to boil the goods in milk of lime. This step is viewed by experienced bleachers as one of the most important ones in the process. The lime seems to have a marked effect on certain coloring matters in the fibre as well as upon certain stains incident to the process of the manufacture of the

cloth. After the goods have been sufficiently boiled in lime, the liquid that is poured away has a dark brown color, which, of itself, serves as a significant indication of the amount of coloring matter removed from the cloth. Of course it must not be forgotten that the *lime-boil* is but a single stage in the process of bleaching. The later ones consist in the application of dilute acid, of solution of soda-ash, sodium carbonate, Na_2CO_3, of a solution of bleaching powder. These operations are essential to the completion of the process which the lime has begun.

3 — Lime finds another important use in the manufacture of bleaching powder, which, as the preceding remarks show, is an article which is consumed in enormous quantities.

4 — Further, in a great many industries that may be classed more distinctly as chemical, quicklime is largely used because of its properties as a cheap and effective substance, not exactly alkaline, but of alkaline type.

5 — The union of water with lime is attended with considerable expansion, the new product occupying more space than the old one. An interesting application of this property has recently been made in some English coal mines. Quicklime being pressed into a cartridge and the cartridge inserted in a hole drilled in the coal, a small quantity of water is forced into suitable apertures in the lime; the slow but powerful swelling of the mass, results in the lifting off of great blocks of coal, and with less waste in the way of small coal than attends the use of gunpowder blasting.

Calcium sulphide, CaS. — This compound may be produced by heating calcium sulphate, $CaSO_4$, with carbon; the carbon withdraws oxygen, *reducing* the sulphate to a sulphide.

The sulphide is of considerable interest on account of its property of absorbing light in the daytime, and afterwards emitting it during the period of darkness. In the first portion of the dark period the light is of a bluish or lavender hue; later it is white. It is said that after ten seconds' exposure to diffused daylight, absorption is as effectual as after an exposure of ten hours. Subsequently light is emitted for ten or twelve hours, and does not entirely cease for thirty hours. The absorption of the light is mainly superficial. It is said that the luminous power continues unimpaired for a period greater than five years.

Fig. 58. Objects painted with calcium sulphide, (luminous paint) give out, in darkness, light absorbed in daylight.

Calcium sulphate, $CaSO_4$. — Calcium sulphate is often found in mineral forms. These occur as white masses which receive different names in accordance with slight variations in chemical composition or crystalline structure. Thus, calcium sulphate is often found in the earth in the form of the mineral known as anhydrite, having the composition expressed by the formula, $CaSO_4$. The same chemical compound often occurs in nature in a state of combination with water; it is then expressed by the formula, $CaSO_4 \cdot 2H_2O$. This hydrated calcium sulphate is called sometimes gypsum, sometimes selenite, according to the crystalline form it assumes.

Gypsum possesses certain valuable properties which bring it into extensive use. Thus, when gently heated in a kiln or furnace constructed for the purpose, the gypsum allows the water that is combined within it, to escape as vapor, but it still retains the form of a white powder. To this the name plaster of Paris has been given. This plaster has the interesting and valuable property of chemically uniting with water again, and then quickly hardening into an entirely solid mass. This property of the substance leads to its wide employment to afford a smooth white surface to the ceilings and inner walls of buildings. It is also often used for producing models of various sorts — from the plaster casts of large statues and architectural objects down to those of coins and medals.

Calcium carbide, CaC_2. — Calcium carbide has been produced recently in very large quantities by the action of an electric arc upon a mixture of coke and quicklime. The product is a gray semifused solid.

When calcium comes in contact with water at ordinary temperatures it reacts as follows:

$$\underset{\text{Calcium carbide}}{CaC_2} + 2H_2O = CaO_2H_2 + \underset{\text{Acetylene}}{C_2H_2}$$

The acetylene produced is a colorless gas which is rather difficult to produce in a pure form otherwise, and which burns with a flame of high luminosity.

Calcium carbonate, $CaCO_3$. — This substance is found in the earth in a number of valuable mineral forms. Perhaps the most noteworthy of them are limestones and marble. While the ancients were familiar with these materials and used them largely for building purposes, they did not as clearly distinguish marble

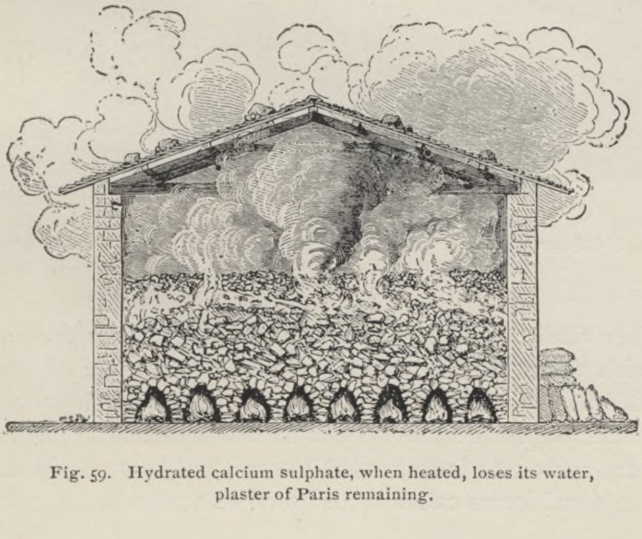

Fig. 59. Hydrated calcium sulphate, when heated, loses its water, plaster of Paris remaining.

Fig. 60. Calcium carbonate, dissolved from overlying soil, reprecipitates in a grotto, as stalactites and stalagmites.

from other similar building stones as we do at the present day. Thus, with them almost any white mineral capable of taking a fine polish was called *marble*. With the moderns, however, the term is reserved for certain special forms of calcium carbonate.

Calcium carbonate is somewhat known, but less widely used, in certain mineral forms called spars, such as Iceland spar, calc spar, etc. It also exists in the earth in large quantities in the white, powdery substance familiarly known as chalk.

Calcium carbonate often appears in grottoes and caves in the earth, in the beautiful and fantastic forms which stalactites and stalagmites assume. When the earth above the roof of the grotto contains considerable limestone, the calcium carbonate is frequently dissolved in the water which penetrates the soil. This solution is effected principally by the aid of carbon dioxide, with which such water is often charged. When, however, the solution reaches the natural ceiling of the cave and drops to the floor beneath, there is a tendency to the escape of carbon dioxide. But the latter agent was that which chiefly accomplished the solution of the limestone. Upon its escape, therefore, the limestone itself reappears, this time, however, in the form of minute particles which deposit themselves slowly, but gradually, in the beautiful shapes of pendant columns which adorn many of the caves visited by travellers.

Appendix to Calcium.—Bleaching-powder.

The substance known as bleaching-powder may be spoken of in a general way as consisting of lime saturated with chlorine. This description points very justly to the method of producing the substance, but gives no idea of the chemical arrangement of the constituents.

Scheele early noticed that chlorine gas possesses decided bleaching power, and the French chemist, Berthollet, soon called attention to the possible applications of the substance in the bleaching industries. But its annoying odor made it impracticable to use chlorine on any large scale in the state of gas, and forbade the use of it even when dissolved in water. At length, twenty years after the discovery of the gas—that is, in 1798—the plan of absorbing chlorine in lime was hit upon, and here may be discovered the beginnings of the bleaching-powder industry, now one branch of the alkali trade, the greatest chemical industry conducted by man. This bleaching-powder, at first a mere chemical curiosity, is now manufactured by the thousands of tons, and is used in the bleaching of cotton and linen goods, both in the form of cloth and in the form of the various kinds of paper.

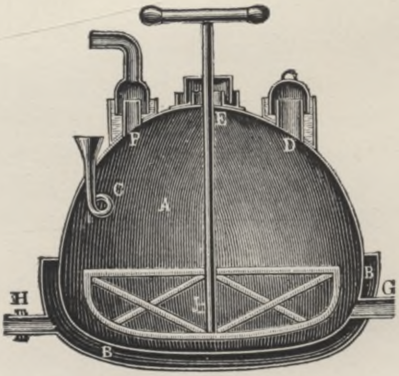

Fig. 61. Old-style chlorine still. Common salt, sulphuric acid, and manganese dioxide are introduced into the still. The mixture is agitated by means of the stirrer; it may be heated by passing steam into the jacket B by the pipe H.

The Preparation of Bleaching-powder.

First stage. — Quicklime is slaked, i. e., to it is added a certain quantity of water sufficient to form calcium hydroxide, and yet to leave this substance as a dry powder. The latter condition seems to be essential to the subsequent successful preparation of bleaching-powder.

Second stage. — Chlorine gas is produced. It is liberated by the action of hydrochloric acid upon manganese dioxide. (The hydrochloric acid is commonly derived by the addition of sulphuric acid to common salt in the preparation of salt-cake for the Leblanc soda-ash process.)

The chemical change is represented by the following equation :

$$MnO_2 + 4HCl = Cl_2 + 2H_2O + MnCl_2$$

This method is the same as that employed on a small scale in the laboratory. In manufacturing, the operation is conducted on a larger scale in great retorts constructed of lead — or in some places, of slabs of stone bolted together.

For a long time it was the custom of manufacturers of bleaching-powder to throw away the manganous chloride, $MnCl_2$, produced in this process. At length Mr. Walter Weldon worked out a successful method of restoring it to the form of manganese dioxide, suitable for use again. In Weldon's process the manganous chloride is treated in suitable tanks with quicklime and large volumes of atmospheric air; the lime withdraws the chlorine, forming calcium chloride, which is thrown away, while the oxygen of the air changes the manganese to dioxide, MnO_2.

Third stage. — The chlorine is made to combine with the dry slaked lime. This operation is conducted in large chambers, in which lime is spread upon the floor or upon shelves, it being arranged in furrows and ridges with a view of exposing a larger surface to the action of the gas. After the lime has been properly spread in these chambers, chlorine gas is allowed to enter in sufficient quantity to fill them. It is then left to stand in contact with the lime for two or three days. As a result a considerable portion of the gas is absorbed. If, upon now testing some of the powder, it is found not yet fully saturated with gas, chlorine is again supplied to the chamber and allowed to remain there for another period of two or three days. The lime is usually then found to have absorbed so much chlorine as will make up somewhere from thirty to forty per cent. of the bleaching-powder produced.

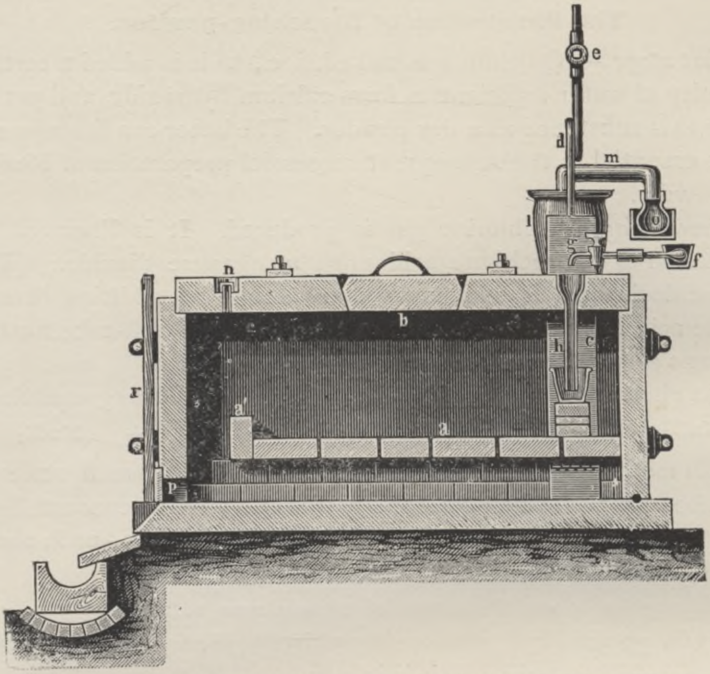

Fig. 62. Longitudinal vertical section of English chlorine still, made of slabs of stone. Manganese dioxide, and hydrochloric acid (introduced at *g*) liberate chlorine (which is conducted away by *m*).

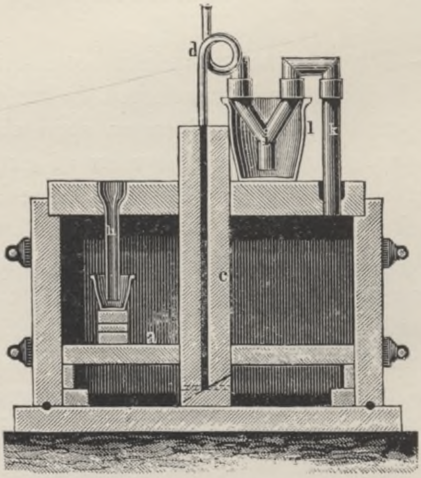

Fig. 63. Transverse vertical section of English chlorine still (same as Fig. 62). (The chlorine gas goes out at *k*; it is washed in the jar *l*).

While, as already intimated, the exact composition of bleaching-powder has not yet been conclusively made out, it is sufficient for all ordinary purposes to consider it as a combination of three compounds which may be expressed thus :

$CaCl_2O_2$	+	$CaCl_2$	+	CaO_2H_2
Calcium hypochlorite		Calcium chloride		Calcium hydroxide

It must be admitted to be the fact that all ordinary chemical changes in which bleaching-powder takes part, may be *expressed* without consideration of the calcium hydroxide given in the formula. This latter substance, however, appears to be always present in bleaching-powder. It is proper, therefore, to take it into account in the more exact expressions for this substance.

The liberation of chlorine from bleaching-powder by sulphuric acid is represented by the following equation :

$CaCl_2O_2 + CaCl_2$	+	$2H_2SO_4$	=	$2CaSO_4$	+	$2H_2O$	+	$2Cl_2$
Bleaching-powder		Sulphuric acid		Calcium sulphate		Water		Chlorine gas

The use of bleaching-powder offers certain advantages. The following are some of them :

— The compound is itself white.

— It is a solid which can be easily handled, packed, and transported.

— With reasonable precautions the active bleaching agent, chlorine, is retained by the powder in available form for a considerable length of time.

— The liberation of this chlorine is easily effected. The addition of almost any acid will accomplish it ; even the carbon dioxide of the atmosphere will suffice.

— In actual use in the process of bleaching, the entire amount of chlorine originally stored up in the powder may be liberated in contact with the goods to be bleached.

In the bleaching of cotton goods chlorine is not the only agent relied upon, though it seems to be an essential one. At least three other substances are employed to contribute to the bleaching. Each of them either removes some colors or stains from the goods or so modifies them that the solution of bleaching-powder — one of the last agents to be employed — can the easier finish its work. The three substances referred to are milk of lime, diluted sulphuric acid, and sodium carbonate, also called soda-ash.

The pieces of cloth, being sewed together in continuous strips many miles in length, pass from one liquor to another, with washings in water at proper times, until finally, after being fully whitened by the chlorine preparation and then receiving the final washing in water, they emerge from the works, completely bleached.

STRONTIUM; Sr; 87,61.

Introduction — Distribution, preparation, properties and compounds of strontium.

Data for Reference.

Density of solid strontium, 2.5 (water being the standard = 1).

Solid strontium fuses at a bright red heat.

Boiling point of liquid strontium is between that of calcium and barium.

A strontium compound was discovered in 1787 as a new mineral; in 1794 Hope showed that it contained a new metal.

Strontium, as a new metal, was first isolated by Sir Humphry Davy in 1808.

The word strontium is derived from Strontian, a village in Argyllshire, Scotland.

Introduction.

Strontium and its compounds bear many marked resemblances to barium and its compounds. But strontium compounds when highly heated give out red light while barium compounds give out green light.

Distribution of Strontium.

Strontium has not been found in the free state in nature. The chief natural compounds recognized are the mineral strontianite, strontium carbonate, $SrCO_3$, and the mineral celestite (also called celestine), strontium sulphate, $SrSO_4$.

Preparation and Properties of Strontium.

The metal may be prepared by electrolysis of fused strontium chloride. It is a pale-yellow metal resembling calcium in that it does not oxidize in dry air, and that it easily decomposes water at ordinary temperatures.

A Few Compounds of Strontium.

With fluorine;	Strontium fluoride,	SrF_2	
With chlorine;	——— chloride,	$SrCl_2$	
With bromine;	——— bromide,	$SrBr_2$	
With iodine;	——— iodide,	SrI_2	
With oxygen;	——— oxide,	SrO;	Strontium hydroxide, SrO_2H_2
	——— dioxide,	SrO_2	

With sulphur;	Strontium sulphide,	SrS;	Strontium hydrosulphide,	SrS_2H_2
	—— tetra ——	SrS_4;	—— sulphate,	$SrSO_4$
	—— penta ——	SrS_5		
With selenium;	Strontium selenide,	SrSe		
With nitrogen;	Strontium nitride,	Sr_2N_2:	Strontium nitrate,	$Sr(NO_3)_2$
With carbon;			Strontium carbonate,	$SrCO_3$
With silicon;	Strontium silicofluoride,	$SrSiF_6$		

Strontium nitrate. — This is the principal commercial salt of strontium ; its chief use is in fireworks. This use is based on the fact that any compound of strontium when sufficiently heated, affords light of a splendid red color.

BARIUM; Ba; 137,43.

Introduction — Distribution, preparation, and properties of barium — Barium compounds, especially the chloride, oxide (baryta), sulphate.

Data for Reference.

Density of barium, 3.5 — 4 (water being the standard = 1).
Fusing point of solid barium, unknown.
Barium compounds were first recognized by Scheele, in 1774.
Barium, as a new metal, was first isolated by Sir H. Davy, in 1808.
The word barium is derived from a Greek word, βαρύς (*barys*), heavy.

Introduction.

Scheele in 1774 studied the black mineral now known as pyrolusite, manganese dioxide, MnO_2. His sample was somewhat impure and he recognized that it contained several different substances, among others a compound of a new metal — that which is now called barium. But Scheele was not able to isolate the metal.

Distribution of Barium.

Barium has not been found in the free state in nature. The chief natural compounds recognized are the mineral barite (also called heavy spar), barium sulphate, $BaSO_4$, and the mineral witherite, barium carbonate, $BaCO_3$.

Preparation and Properties of Barium.

Barium may be prepared in an impure form by electrolysis of fused barium chloride, $BaCl_2$.

As it is difficult to prepare pure barium, its properties in the metallic form are not definitely known. It appears to decompose water at ordinary temperatures.

A Few Compounds of Barium.

With fluorine;	Barium fluoride,	BaF_2		
With chlorine;	——— chloride,	$BaCl_2$;	Barium chlorate,	$Ba(ClO_3)_2$
	——— fluochloride,	$BaFCl$		
With bromine;	——— bromide,	$BaBr_2$		

With iodine;	——— iodide,	BaI_2;	Barium iodate,	$Ba(IO_3)_2$
With oxygen;	Barium oxide,	BaO;	Barium hydroxide,	BaO_2H_2
	——— dioxide,	BaO_2		
With sulphur;	Barium sulphide,	BaS;	Barium hydrosulphide,	BaS_2H_2
	——— tri ———	BaS_3;	——— sulphate,	$BaSO_4$
	——— tetra ———	BaS_4;	——— disulphate,	BaS_2O_7
			——— dithionate,	BaS_2O_6
With selenium;	Barium selenide,	$BaSe$		
With nitrogen;	——— nitride,	BaN_6;	Barium nitrate,	$Ba(NO_3)_2$
With phosphorus;	——— phosphide,	BaP_2		
With carbon;			Barium carbonate,	$BaCO_3$
With silicon;	Barium silicofluoride,	$BaSiF_6$		

Barium chloride, $BaCl_2$. — This compound may be prepared by dissolving witherite in hydrochloric acid. It is often prepared from barite as follows: the barite is heated with carbon, which reduces the barium sulphate, $BaSO_4$, to barium sulphide, BaS; then the barium sulphide is dissolved in hydrochloric acid.

Barium chloride is an important reagent in the chemical laboratory; it is used in the detection of sulphates.

Barium sulphide, BaS, may be prepared from barite as described under barium chloride. Like calcium sulphide, on exposure to sunlight, it absorbs certain of the rays, emitting them in the dark.

As early as 1602, Vincentius Casciorolus, a shoemaker of Bologna, observed this fact. He called his product *lapis solaris*, and it soon created wide-spread and long-continued interest, under the name of *Bolognese phosphorus*.

Barium sulphate, $BaSO_4$, is a white solid, highly insoluble in water and other reagents.

Barium sulphate is largely used in the arts as a white pigment. It has considerable weight, and its unchangeability under the influence of water and many other substances, are properties which fit it for the use mentioned. Thus it is employed, mixed with white lead, in the cheaper kinds of white paint. Under the name of *blanc fixe*, it is also used to give color and weight to paper and to cotton goods and to many other commercial articles which require a smooth, hard, white surface.

BERYLLIUM; Be (or Glucinum; Gl) 9,08.

Distribution, preparation, properties, and compounds of beryllium.

Data for Reference.

Density of solid beryllium, 1.85 (water being the standard = 1).

Fusing point of solid beryllium, above 772° C.

Beryllium oxide was recognized, as a new and special substance, as early as 1797.

Metallic beryllium was first prepared by Friedrich Wöhler in 1827.

The name beryllium is derived from *beryl*, which in turn is derived from a foreign Greek word, βήρυλλος (*beryllos*), a crystal.

Beryllium is sometimes called glucinum, a word derived from the Greek word γλυκύς (*glykys*), meaning sweet (referring to a sweetish taste possessed by certain of its compounds).

Distribution. — Beryllium exists in the earth in small quantities in the mineral beryl and a few other silicates.

Beryl has long been known. Its use as a gem is referred to in the Bible. It is found somewhat widely distributed in the earth as a mineral, sometimes massive, sometimes in well-defined crystals. It is a double silicate of aluminium and beryllium, having the formula, $3BeO \cdot Al_2O_3 \cdot 6SiO_2$.

Preparation. — The metal beryllium was not obtained as a pure substance until 1827, when the German chemist Wöhler produced it. The method employed by him resembled that he had followed in producing certain other metals, aluminium, for instance, i. e., he displaced the metal beryllium from its compounds by the use of potassium. Later, the French chemist Debray obtained a yet finer grade of metal by the use of sodium instead of potassium.

Properties. — Beryllium exists as a steel colored metal. It is very hard. It forms crystals of the hexagonal system. It does not readily combine with oxygen in the air. At very high temperatures, however, as that afforded by the oxyhydrogen blowpipe, beryllium combines with oxygen to form an oxide.

A Few Compounds of Beryllium.

With fluorine;	Beryllium fluoride, BeF_2 (?)	
With chlorine;	——— chloride, $BeCl_2$	
With bromine;	——— bromide, $BeBr_2$	
With iodine;	——— iodide, BeI_2	
With oxygen;	Beryllium oxide, BeO;	Beryllium hydroxide, BeO_2H_2
	——— oxychloride, Be_2OCl_2	
With sulphur;	(Sulphide doubtful)	Beryllium sulphate, $BeSO_4$
With phosphorus;		Beryllium phosphate, $Be_3(PO_4)_2$
With carbon;		Beryllium carbonate, $BeCO_3$

MAGNESIUM; Mg; 24,28.

Introduction — Distribution, preparation, properties, and compounds of magnesium.

Data for Reference.

Density of solid magnesium, 1.75 (water being the standard = 1).
Fusing point of solid magnesium, 433° C.
Boiling point of liquid magnesium, 929°—954° C.
Metallic magnesium was produced first by Sir Humphry Davy in 1800
The word magnesium is derived from Magnesia, an ancient name for Asia Minor.

Introduction.

The famous electrolytic experiments of Sir Humphry Davy, led to the production by him of the metals potassium, sodium, barium, strontium, calcium, and also magnesium.

Salts of magnesium were known long before the metal itself was recognized; but for a time *magnesia alba*, containing our true magnesium, was confused with *magnesia nigra*, a name applied at first to natural manganese dioxide, called in mineralogy *pyrolusite*. In order to avoid this confusion, the metal contained in *magnesia alba* was called magnesium, and that in *magnesia nigra*, manganese.

Distribution of Magnesium.

The element magnesium does not occur in the earth in the free or uncombined form; but in the form of chemical compounds of one sort or another, magnesium is very abundant; indeed it is the sixth element in the order of quantity by weight in the earth.

Magnesium exists in many minerals:

1st — *Magnesite*, magnesium carbonate, $MgCO_3$; *dolomite*, double carbonate of magnesium and calcium, $(MgCa)CO_3$; *kieserite*, magnesium sulphate, $MgSO_4,H_2O$.

2d — Certain Stassfurt minerals are worthy of mention here although they are referred to more at length under the head of potassium. They are the following:

Carnallite	$MgCl_2 \cdot KCl\ 6H_2O$
Kainite	$K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$

3d — Magnesium also occurs in an important group of silicious minerals, of which the following may be mentioned :

Asbestos	$(MgCa)SiO_3$
Talc	$H_2Mg_3Si_4O_2$
Meerschaum	$H_2Mg_2Si_3O_9 \cdot H_2O$

4th — Magnesium is also found as an important constituent of a great many other minerals.

5th — Compounds of magnesium exist in sea water and in the waters of many mineral springs.

Preparation of Magnesium.

The method commonly employed at present for producing metallic magnesium depends upon the superior chemical affinity of metallic sodium. When sodium is heated with certain compounds of magnesium, magnesium is expelled by the sodium.

Properties of Magnesium.

The metal magnesium has a silver white color. It is capable of being drawn into wire, and the wire is sufficiently malleable to be afterward rolled into ribbon.

Magnesium does not oxidize in dry air. It is acted upon somewhat by moist air — more by hot water. It easily dissolves in the common acids.

A fragment of wire or ribbon, or a portion of the pulverized metal, easily takes fire from a lighted match or burning candle, and the metal in burning gives out a dazzling white light, which is very rich in rays possessing chemical activity. This light has been used in the photography of dark interiors, like those of the Roman catacombs and the Egyptian pyramids. In burning, the magnesium combines with the oxygen of the air, and so gives rise to a white ash: magnesium oxide, MgO.

A Few Compounds of Magnesium.

With fluorine;	Magnesium fluoride, MgF_2	
With chlorine;	——— chloride, $MgCl_2$;	Magnesium potassium chloride, $MgCl_2\cdot KCl$
		——— ammonium ——— $MgCl_2\cdot NH_4Cl$
		——— calcium ——— $2MgCl_2\cdot CaCl_2$
With bromine;	——— bromide, $MgBr_2$	
With iodine;	——— iodide, MgI_2	
With oxygen;	Magnesium oxide, MgO;	Magnesium hydroxide, MgO_2H_2

With sulphur;	Magnesium sulphide, MgS;	—— hydrosulphide, MgS_2H_2 —— sulphite, $MgSO_3$ —— sulphate, $MgSO_4$
With boron;	Magnesium borofluoride, $Mg(BF_4)_2$	
With nitrogen;	—— nitride, Mg_3N_2;	Magnesium nitrate, $Mg(NO_3)_2$
With arsenic;	—— arsenide, Mg_3As_2	
With phosphorus;	—— phosphide, Mg_3P_2;	—— phosphate, $Mg_3(PO_4)_2$ —— hydrogen —— $MgHPO_4$ —— ammonium —— $Mg(NH_4)PO_4$
With carbon;		Magnesium carbonate, $MgCO_3$
With silicon;	Magnesium silicide, Mg_2Si; Another —— Mg_5Si_3	(many complex silicates)

Magnesium oxide (magnesia), MgO, is a white powder very light in weight, often called calcined magnesia. It is produced by heating magnesium carbonate. The heat expels the carbon dioxide. Magnesium oxide easily unites with acids. Thus it acts like a mild alkali. It is used in medicine for the purpose of neutralizing acidity.

Magnesium sulphate (Epsom salts), $MgSO_4 \cdot 7H_2O$, is a white crystalline salt. It is used somewhat in medicine.

Asbestos, a magnesium mineral, is considerably employed for a multitude of purposes where a fire-proof material is desired. Thus, the more fibrous varieties are used for non-consuming lamp-wicks, and for fire-proof drop-curtains for theatres. The varieties having shorter staple are employed for the manufacture of fire-proof paints; for the manufacture of a kind of pasteboard for use on flooring and for covering steam-pipes, boilers, etc.

ZINC; Zn; 65, 41.

Distribution, extraction, properties, uses, and compounds of Zinc.

Data for Reference.

Density of solid zinc, 6.9 (water being the standard = 1).

Fusing point of solid zinc, 433.3° C.

Boiling point of liquid zinc, 929°—954° C.

Density of zinc vapor, 34.35 (hydrogen gas being the standard = 1).

One litre of zinc vapor weighs 3.08 gms., (at 0° C., and barometric pressure of 760 m. m. of mercury.)

Distribution of Zinc.

Zinc is not found, free or uncombined, in the earth. Its principal ores are:

Zinc blende (also called black-jack), zinc sulphide, ZnS,
Smithsonite (calamine), zinc carbonate, $Zn\,CO_3$,
Silicious calamine, zinc silicate, $Zn_2\,SiO_4\,H_2O$.

Extraction of Zinc.

There are two principal methods of producing zinc from the ore: the Belgian method and the Silesian method. They both depend upon the same principles. They accomplish the separation of the metal, however, by slightly different mechanical contrivances.

In both methods the ores are subjected to a preliminary roasting. When carbonated calamine is roasted, carbon dioxide is expelled and zinc oxide remains. When blende is roasted, the oxygen of the air burns off the sulphur, in part, at any rate, leaving the zinc oxide together with some zinc sulphate.

In the *Belgian system*, the roasted ore is mixed with finely powdered coal or with charcoal. The mixture is introduced into earthenware retorts. A large number of these retorts is placed in a tall furnace. Each retort is provided with a long neck projecting in front of the furnace. The heat of the furnace enables the carbon to deprive the ore of oxygen. Thus the zinc is liberated. It flows down the inclined retort towards the neck. If any

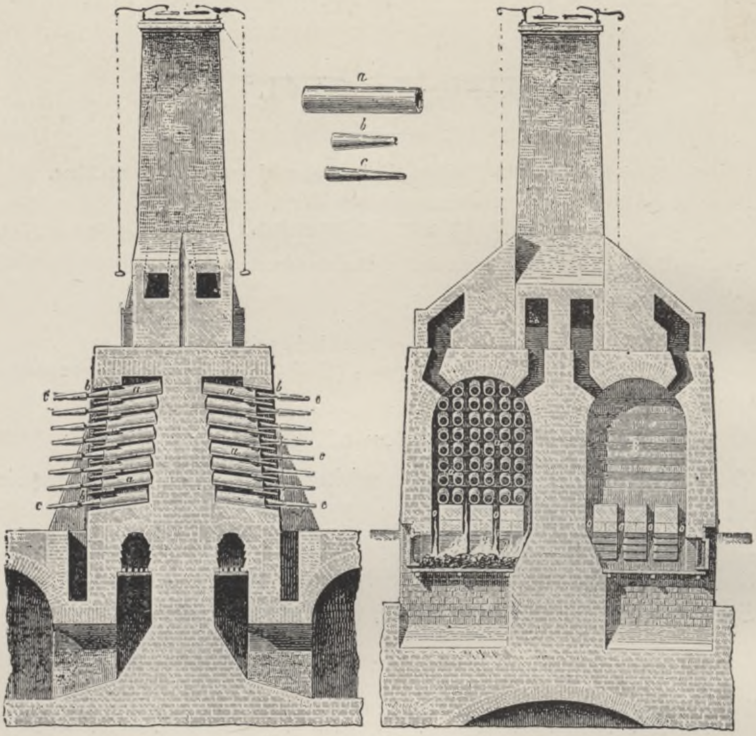

Fig. 64. Two vertical sections of a Belgian zinc furnace.

zinc burns in such air as comes in contact with it, white oxide of zinc is formed; and this collects in the necks. When the process is judged to be sufficiently advanced, the necks are removed and a workman scrapes the melted zinc from the retort into an iron ladle or ingot mold. Such oxide of zinc as collects in the necks is added to a subsequent charge of mixture to be placed in the retorts.

The smelting of zinc ores for the production of the metal (commonly called spelter) or for the manufacture of oxide of zinc, is now carried on in the United States in three sections. In Pennsylvania and New Jersey, both spelter and oxide are produced, but the latter in larger quantities. In Virginia and Tennessee, smaller quantities of spelter are produced, but practically no oxide. In Kansas, Illinois, Wisconsin, and Missouri, the chief product is spelter. The Western districts are the most productive.

Uses of Metallic Zinc.

— In *galvanic batteries*, zinc is considerably used; indeed the chief source of the electric energy is, in this case, referable to the chemical action between the zinc and the solution used in the galvanic cell.

— In many alloys like *brass* and *bronze*, zinc is used. Brass is an alloy of copper and zinc. In its manufacture it is customary to melt the copper first. Then the zinc is dropped into the melted copper. It dissolves quickly, diffusing throughout the mass. Bronze differs from brass mainly in the fact that it has some tin added to the alloy.

Certain ornamental objects made of zinc and afterwards colored on the outer surface, are sold under the name of *French bronze*. The metal is cheaper than bronze, and, moreover, it assumes the liquid condition at such a low temperature that it easily fills all the fine lines of the mold.

The name *galvanized iron* is applied to iron coated with a thin film of metallic zinc. In the preparation of galvanized iron a tank of melted zinc is provided. On the surface of the zinc a thick coating of ammonium chloride, NH_4Cl, is spread, in order to protect the surface of the zinc from oxidizing in the air. The iron which is to be coated, is first cleansed with acid, or else it is furnished with a thin layer of metallic tin. Afterward, it is dipped in

Fig. 65. When metallic zinc is heated, it melts, vaporizes, and oxidizes (affording flame, and producing a white smoke composed of solid particles of zinc oxide, ZnO).

the tank of melted zinc; thereupon the latter metal clings to the surface. Upon withdrawing the iron, it is found thoroughly coated.

Many zinc salts are distinctly poisonous. When galvanized iron vessels are employed to hold drinking water, or even when galvanized iron water pipes are used, there is a danger that some of the zinc will be introduced into the water; thus injury may be done to the health of persons who drink the water.

Properties of Zinc.

Zinc is a bluish-white metal possessing a brilliant metallic lustre. When in ingots, it displays distinct crystalline tendencies. The latter are more marked when the ingots are broken.

Zinc easily oxidizes on exposure to moist air, and acquires a white coating of zinc oxide, ZnO.

When zinc is heated to the point of fusion, it vaporizes and even burns, producing a brilliant white light, and at the same time abundant masses of white smoke, consisting of minute particles of zinc oxide, ZnO. In certain fireworks, powdered zinc is employed to produce effects dependent upon this principle.

Zinc easily dissolves in the stronger acids, producing salts.

A Few Compounds of Zinc.

With chlorine;	Zinc chloride,	$ZnCl_2$		
With bromine;	——— bromide,	$ZnBr_2$		
With iodine;	——— iodide,	ZnI_2		
With oxygen;	Zinc oxide,	ZnO;	Zinc hydroxide;	ZnO_2H_2
With sulphur;	——— Sulphide;	ZnS;	——— sulphate,	$ZnSO_4$
	——— pentasulphide,	ZnS_5		
With nitrogen;	Zinc nitride,	Zn_3N_2;	Zinc nitrate,	$Zn(NO_3)_2$
	——— amide,	$Zn(NH_2)_2$;	——— nitrite,	$Zn(NO_2)_2$
With phosphorus;	——— phosphide	Zn_3P_2;	——— phosphate,	$Zn_3(PO_4)_2$
With carbon;			Zinc carbonate,	$ZnCO_3$
	Zinc cyanide,	$Zn(CN)_2$;		

Zinc-white.—Oxide of zinc, under the name of zinc-white, is sometimes mixed with oil to form a pigment, to be employed as a substitute for white lead. The advantages of its use appears from the following considerations: When paint containing white lead is employed in places where sulphuretted hydrogen is liberated, the paint becomes blackened or tarnished from the formation of black sulphide of lead, PbS· If the so-called zinc paint is employed under similar conditions, sulphide of zinc, ZnS, may, it is true, be formed; but, in this case, tarnishing does not take place, since the sulphide of zinc is white.

CADMIUM; 111; 95.

Distribution, preparation, properties, uses, and compounds of cadmium.

Data for Reference.

Density of solid cadmium, 8.8 (water being the standard = 1).

Fusing point of solid cadmium 320° C.

Boiling point of liquid cadmium 763°-772° C.

Density of cadmium vapor 55.8 (hydrogen gas being the standard = 1).

One litre of cadmium vapor weighs 4.999 gms., (at 0° C., and a barometric pressure of 760 m. m. of mercury.)

Cadmium was discovered by Stromeyer in 1817.

The word cadmium is derived from the Greek word *καδμεία* (*kadmeia*), calamine (an ore of zinc).

Distribution of Cadmium.

Cadmium is a comparatively rare metal. It occurs in nature in the mineral greenockite, cadmium sulphide, CdS, in Pennsylvania, and also in some parts of Europe. It ordinarily occurs associated with zinc, in certain ores of the latter metal, especially those found in Silesia.

Preparation of Cadmium.

— In the distillation of crude zinc oxide with charcoal, any cadmium, if present, tends to separate from the zinc, for the cadmium is more volatile than the zinc: thus cadmium compounds may be found in the flues in which furnace products condense.

When zinc oxide contains some cadmium oxide, the two may be separated by wet processes. When the cadmium oxide has been obtained in a nearly pure form, it may be decomposed by means of charcoal under the influence of heat, by use of a suitable retort. The charcoal withdraws oxygen from the cadmium, and the metal, as a vapor, distils, condensing in the receiver.

Properties of Cadmium.

Cadmium is a bluish-white metal, soft, malleable, and ductile. Upon heating in the air it oxidizes, burning into cadmium oxide, CdO.

Uses of Metallic Cadmium.

The metal cadmium is somewhat used in the arts in fusible alloy. An alloy of tin, bismuth, lead and cadmium, fuses at a temperature of about 160° F. By varying the proportions of the constituents, the fusing point may be raised.

Such an alloy is used in the automatic sprinklers employed for the fire protection of mills. The mill is provided with a series of water pipes, distributed as a net work over the ceilings of the rooms to be protected, At proper points, the water pipes are provided with outlets. These outlets are closed by valves which are kept in place by levers soldered with fusible alloy. If, now, a fire starts, it quickly raises the temperature of the surrounding air to a point sufficient to melt the fusible alloy. The valve then opens, and the water is sprinkled about in sufficient quantity to extinguish the incipient conflagration.

A Few Compounds of Cadmium.

With fluorine	Cadmium fluoride,	CdF_2		
With chlorine;	——— chloride,	$CdCl_2$		
With bromine;	——— bromide,	$CdBr_2$		
With iodine;	——— iodide,	CdI_2		
With oxygen;	Cadmium oxide,	CdO;	Cadmium hydroxide,	CdO_2H_2
With sulphur;	——— sulphide,	CdS;	——— sulphate,	$CdSO_4$
			——— sulphite,	$CdSO_3$
With selenium;	——— selenide,	$CdSe$		
With tellurium;	——— telluride,	$CdTe$		
With nitrogen;	Cadmium nitride,		Cadmium nitrate,	$Cd(NO_3)_2$
			——— nitrite,	$Cd(NO_2)_2$
With arsenic;	——— arsenide			
With carbon;			Cadmium carbonate,	$CdCO_3$
With silicon;	Cadmium silicofluoride,	$CdSiF_6$;		

Cadmium iodide, CdI_2, is a white substance, somewhat used in photography.

Cadmium sulphide, CdS, is a yellow substance, somewhat used as a pigment.

MERCURY; Hg; 200.

Introduction — Distribution, preparation, properties, and compounds of mercury.

Data for Reference.

Density of solid mercury 14.93 (water being the standard = 1).
" " liquid " 13 59 " " " "
Fusing point of solid mercury — 39.4° C.
Boiling point of liquid mercury 357° C.
Density of mercury vapor 99.9 (hydrogen gas being the standard = 1).

One litre of mercury vapor weighs 8.95 gms., (at 0° C. and barometric pressure of 760 m. m. of mercury.)

Mercury was known as early as the first century, A. D.

The word mercury is derived from the name of the Roman divinity Mercurius. The symbol Hg is abbreviated from a word of Latin structure, hydrargyrum, the latter word coming from two Greek words ὕδωρ (*hydor*), water, and ἄργυρος (*argyros*), silver, meaning liquid silver.

In every-day life mercury is often called quicksilver (early signification of quick = living).

Introduction.

The supply of mercury is derived from Europe (Spain, Austria, Italy, and lately from Russia, the Russian deposit being near Nikitowka, in the Donetz basin), the United States (California), Mexico and Canada.

The world's output is nearly stationary, but that of the United States has of late fallen off somewhat, while that of other countries has increased moderately.

The chief avenues of consumption for mercury in the arts, are in connection with the securing of gold and silver from their ores. Another very important use is in the manufacture of mirrors, the coating employed being an amalgam of mercury and tin. In small quantities it is employed as an amalgam with cadmium as a filling for teeth. Small quantities are also employed in medicine in the form of mercurial ointment and blue pill.

Considerable quantities of mercury are consumed in the manufacture of compounds of the metal. In the arts, the chief compound employed is vermilion, a scarlet pigment. It is mercuric sulphide, HgS. It is largely used in oil paints and by the Chinese and Japanese in red lacquers.

Distribution of Mercury.

1 — Mercury is found in the earth in the free and uncombined condition called native mercury; that is, as globules distributed through earth or mineral matter. In this condition, it exists in some parts of Germany, in Peru, and in California.

2 — Mercury also occurs in the earth in the sulphide called cinnabar, mercuric sulphide, HgS, in Idria, Almaden in Spain, and New Almaden in California. Cinnabar varies in color from red to brown.

Preparation of Mercury.

The preparation of mercury from the ore is conducted at Idria somewhat as follows:

A furnace is constructed consisting of a central part and wings. In the central part is a fire, adjusted to heat and roast the ore. In the wings are circuitous passages for the condensation of vapors. The ore, in connection with fuel, being charged into the furnace, the fires are lighted. The sulphur in the ore is turned into sul-

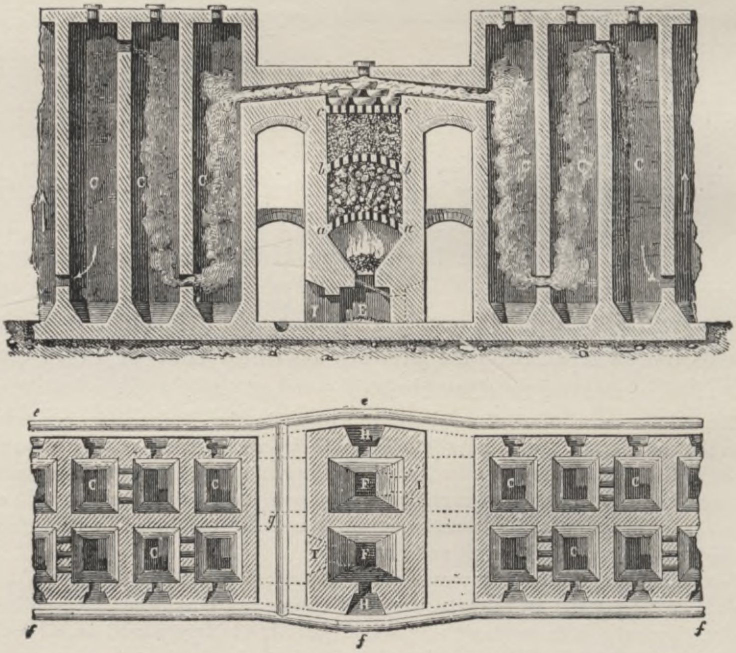

Fig. 66. Furnace for metallurgic extraction of mercury. (System used at Idria.) (The lower diagram represents a horizontal section through the base of the furnace.)

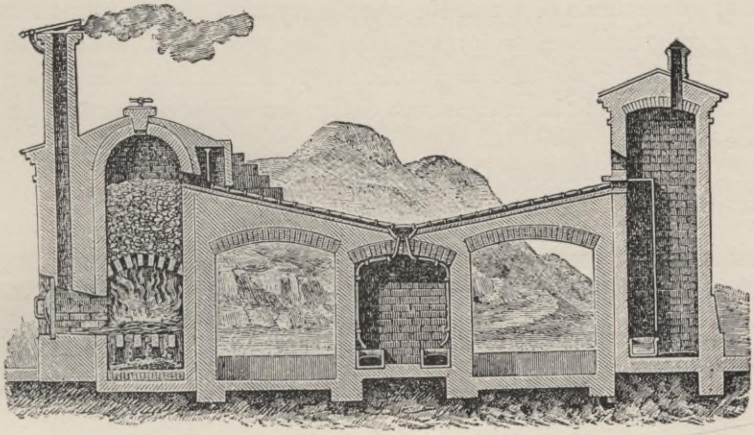

Fig. 67. Furnace for metallurgic extraction of mercury. (Spanish system.)

phur dioxide which passes into the passages and away through the chimney. The mercury is volatilized, condenses in the circuitous passages, and is drawn off by means of a conduit below. The mercury so obtained is cleansed by straining through cloths.

In some cases, the ores mixed with a suitable flux, say limestone, are heated in retorts similar in shape to those of gas works. The lime decomposes the cinnabar, retaining the sulphur. Thereupon, the liberated mercury is vaporized and conveyed by pipes into a sort of hydraulic main containing cold water. The mercury collects at the bottom of the water and is drawn off. It is subjected to subsequent purification when necessary.

Properties of Mercury.

Mercury is a silver white metal, liquid at all ordinary temperatures. It freezes at about 40° below zero F. (at the same number on the centigrade scale, this being the point at which the two scales cross each other). Mercury boils at about 357° C. though it vaporizes in a minute degree even at ordinary temperatures.

This latter property is utilized in natural history cabinets. A small amount of metallic mercury placed in a drawer containing specimens of butterflies, affords sufficient vapor to poison minute parasitic insects which might otherwise injure the specimens. This vaporization may be demonstrated by hanging gold leaf in a vessel containing a little metallic mercury. In a few months, the gold leaf acquires a silvery appearance from the absorption of the mercurial vapors.

Mercury has many striking and important chemical properties : It forms a very large number of known compounds ; these are grouped in two definite series — the *mercurous*, and the *mercuric*.

Many compounds of a notable complexity are known — thus there is a strong tendency to form double compounds of considerable variety. Many of the compounds are possessed of marked colors. Practically all of the compounds easily decompose under the influence of heat.

A Few Compounds of Mercury.

With fluorine;	Mercurous fluoride,	Hg_2F_2		
	Mercuric ———	HgF_2		
With chlorine;	Mercurous chloride,	Hg_2Cl_2;	Mercurous chlorate,	$Hg_2(ClO_3)_2$
	Mercuric ———	$HgCl_2$;	Mercuric ———	$Hg(ClO_3)_2$
			Mercurous perchlorate,	$Hg_2(ClO_4)_2$
With bromine;	Mercurous bromide,	Hg_2Br_2		
	Mercuric ———	$HgBr_2$		
With iodine;	Mercurous iodide,	Hg_2I_2		
	Mercuric ———	HgI_2		
	Another ———	$HgI \cdot HgI_2$		
	Mercuric iodochloride,	$HgICl$		
	Another ———	$HgI_2 \cdot 2HgCl_2$		
	Mercuric iodo chloride,	$HgICl$		
With oxygen;	Mercurous oxide,	Hg_2O		
	Mercuric ———	HgO		
	——— oxyfluoride,	$HgO \cdot HgF_2$		
	Several oxychlorides,	$Hg_xO_yCl_z$		
	——— oxybromide,	$3HgO \cdot HgBr$		
	——— oxyiodide,	$3HgO \cdot HgI_2$		
With sulphur;	Mercurous sulphide,	HgS;	Mercurous sulphate,	Hg_2SO_4
	Mercuric ———	Hg_2S;	Mercuric ———	$HgSO_4$
			——— sulphite,	$HgSO_3$
With selenium;	Mercuric selenide,	$HgSe$		
	——— seleno chloride,	$Hg_3Se_2Cl_2$		
	——— seleno sulphide,	$HgSe \cdot 4HgS$		
With nitrogen;	Mercurous nitride,	Hg_2N_6;	Mercurous nitrate,	$Hg_2(NO_3)_2$
	Mercuric ———	Hg_3N_2;	Mercuric ———	$Hg(NO_3)_2$
	Dimercuric ammonium chloride,	NHg_2Cl		
	Mercuric ——— ———	$NHgH_2Cl$		
	Dimercurous ammonium chloride,	NHg_2H_2Cl		
	Mercuric diammonium chloride,	$(NH_3)_2HgCl_2$		
	Mercurous ——— ———	$(NH_3)_2Hg_2Cl_2$		
With phosphorus;			Mercurous phosphate,	Hg_3PO_4
			(Many other phosphates)	
With carbon;			Mercurous carbonate,	Hg_2CO_3
			(Many other carbonates)	
	Mercuric cyanide,	$HgCN$;	Mercuric cyanate,	$HgO_2(CN)_2$
			——— sulpho ———	$HgS_2(CN)_2$
	Mercury dimethide,	$Hg(CH_3)_2$		
	——— diethide,	$Hg(C_2H_5)_2$		

(Many amalgams with metals, as sodium, potassium, ammonium, copper, silver, cadmium, amalgams)

Mercurous chloride, called calomel, Hg_2Cl_2, is a white substance, insoluble in water, easily produced by the addition of hydrochloric acid or soluble chlorides to solutions of other mercurous salts. It is also produced when mercuric chloride and metallic mercury, intimately mingled, are heated.

Mercuric chloride, called corrosive sublimate, $HgCl_2$, is a white compound soluble in water. It is manufactured by heating mercuric sulphate with common salt. The mercuric chloride formed goes off in vapors which — received in a cool vessel — condense in the form of a white salt, in fact, corrosive sublimate.

It is one of the best antiseptics known ; it has come to be very largely employed as an *antiseptic wash* in surgical practice.

Mercuric oxide, called red precipitate, HgO, is a red powder which may be produced by heating mercury moderately in contact with air or with oxygen. Upon raising the temperature still higher, the oxide dissociates, oxygen being liberated. This latter reaction is the one employed by Priestley in the discovery of oxygen. The substance has a further historical interest from those studies of Lavoisier upon chemical action, and especially oxidation, which led to the overthrow of the phlogistic theory.

Mercuric sulphide, called cinnabar, also vermilion, HgS, is a solid, varying in color from brown to red, and even scarlet. Vermilion is produced for use in the arts by rubbing together mercury, sulphur, potassium hydroxide, and water. By and by the product assumes a brilliant red color, showing chemical combination has sufficiently advanced — thereupon the mass is washed with water, and the precipitate is dried.

Commercial vermilion is sometimes adulterated with other red substances, such as red lead and oxide of iron. Such adulteration is readily detected by heating the suspected sample in a glass tube, closed at one end. If the vermilion is pure, it volatilizes completely. If impurities like those already mentioned are present, they remain as a non-volatile residue.

Mercuric thiocyanate, or mercuric sulphocyanate, $HgS_2(CN)_2$, is a white crystalline salt produced by adding ammonium sulphocyanate to a solution of mercuric nitrate. Mercuric sulphocyanate is decomposed when heated, and produces a very voluminous residue. It is used in making a chemical toy known as Pharaoh's serpents.

BOOK III.—THIRD PERIODIC GROUP.

1st Section.—SCANDIUM, YTTRIUM, LANTHANUM, YTTERBIUM.
2d Section.—ALUMINIUM, GALLIUM, INDIUM, THALLIUM.

General Comments on the Group.

The metals of this group (except aluminium) exist in the earth in very minute quantity (but some of them are very widely disseminated).

Aluminium is very abundant, indeed it is the third *element* in order of abundance on this planet, and it is the most abundant *metal* known.

— While the metals of the First periodic group tend to form compounds after the type M_2O (M representing an atom of metal), for example K_2O; and metals of the Second periodic group tend to form compounds after the type MO, for example CaO ; the metals of the Third, and many of those of later periodic groups, tend to form compounds after the type M_2O_3.

Metals of the First Section.

The metals scandium, yttrium, lanthanum, and ytterbium, have not been well isolated, and their compounds have not been prepared in a state of satisfactory purity, (except perhaps those of lanthanum, prepared by Shapleigh).

These metals exist in the earth in *exceedingly small quantities* ; they often occur *together in rare minerals* ; their chemical properties are *so very similar* that it is almost impossible to discriminate between them satisfactorily.

Metals of the Second Section.

Compounds of aluminium are extremely abundant ; the metal has been prepared in a highly pure condition ; a multitude of its salts have been prepared in pure form.

Compounds of the metals gallium, indium, and thallium, are of exceedingly rare occurrence in the earth ; but the metals have been successfully isolated ; and pure salts of them have been produced.

These results are referable partly to the fact that minerals have been found that contain the *individuals* in a practicable form (i. e., *without presence of other difficult elements*), and to the additional fact that the individual metals themselves have *properties* that are *distinctly recognizable* by methods now known (notably by spectrum-analysis).

The Rare Earths.

The general term "earths" has been applied to the oxides of the metals of the Third periodic group — and to several of those of the Fourth and Fifth groups. The terms "rare earths" and "yttrium group of earths," have been applied to the same oxides, except, of course, to those of aluminium, and perhaps one or two other metals.

The oxides of the yttrium group are of somewhat uncertain nature ; it is difficult to separate them one from another ; it is therefore difficult to prepare them in a state of purity ; while metallic substances may be obtained from a so-called individual oxide, it is not thought that such metal is pure and homogeneous.

Chemists at present accept, though with considerable hesitation in many cases, the substances with the following names as representing elementary substances ;

Scandium,
Yttrium,
Lanthanum,
Ytterbium,
Cerium,
Thorium,
Columbium (or Niobium),
Neodymium,
Praseodymium,
Erbium.

But they do not at present accept the substances with the following names, as distinct elements (although proposed by eminent chemists) ;

Mosandrum,
Phillipium,
Decipium,
Thulium,
Holmium,
Rogerium,
Dysprosium,
Gadolinium,
Lucium.

Minerals Containing the Rare Earths.

The first mineral in which the yttrium earths were found is that called gadolinite, so named from Professor Gadolin, a Finnish chemist, who discovered it in 1794, in the neighborhood of Ytterby, Sweden. This mineral, though still very rare, has since been found in several other localities.

In this mineral, Gadolin detected a new earth, which he called "yttria." But subsequent study of gadolinite has shown that the original "yttria" is a very complex substance. Moreover, many new minerals, more or less rare, containing "yttrium metals," have been discovered and studied. Some of them are referred to on subsequent pages. An inspection of the table below shows that the minerals containing these metals vary considerably in composition, and generally they are complex.

In order to present a somewhat more definite statement of the nature of the minerals allied to gadolinite and samarskite, a table is here presented which shows the results of analytical examination of several examples of this class; but it must be understood that as the difficulties of such analysis are enormous the results need some revision :

Table.

	Gadolinite, Ytterby.	Cerite, Bastnas.	Orthite, Greenland.	Wöhlerite, Hitteroe.	Samarskite, North Carolina.	Yttro-cerite, Sweden.	Euxenite, Norway.
YO_3	34.64	....	....	13.20	11.11	9.11	25.09
Ce_2O_3	2.86	60.99	12.63	8.43	3.95	18.21	3.31
Nd_2O_3 } Pr_2O_3 }	8.38	3.90	....	....	....	....	....
E_2O_3	2.93	....	....	....	....	....	....
La_2O_3	3.21	3.51	5.67	....	....	....	....
	— 52.02	— 68.40	— 18.30	— 21.63	— 15.06	— 27.32	— 28.40
VO_2	....	....	....	7.75	17.03	....	5.22
BeO	6.96	....	....	....	....	....	....
Al_2O_3	....	....	14.03	5.41	....	....	3.12
FeO	9.76	1.46	13.63	2.54	14.07	....	1.98
Fe_2O_3	4.73	....	6.36	....	....	....	....
CaO	.83	1.65	12.12	1.63	....	47.63	....
MgO	.15	....	....	3.92	....	....	....
Na_2O	.38	....	....	....	....	....	....
	— 22.81	— 3.11	— 46.14	— 21.25	— 31.10	— 47.63	— 10.32
Cb_2O_5	....	....	....	18.37	54.81	....	38.58
TiO_2	....	....	....	....	....	....	4.36
SiO_2	21.61	21.35	33.78	34.90	....	....	....
CO_2	....	.83	....	....	....	....	....
HF	....	....	....	....	....	25.03	....
H_2O	1.93	6.31	1.78	2.87	.24	....	....
	— 23.54	— 28.49	— 35.56	— 56.14	— 55.05	— 25.03	— 52.94
	98.37	100.	100.	99.02	101.21	99.98	91.66

— Several minerals, notably monazite, containing the rare metals, have been found in North Carolina, a state generally considered as one of the richest localities in North America, as far as *variety* of minerals is concerned.

Monazite is a phosphate containing thorium in the most convenient form for extraction. (This mineral has recently become of great importance in connection with the making of Welsbach burner mantles. It is referred to later under Thorium.)

— In July, 1886, gadolinite was discovered in Texas, not less than 500 kilos being removed from one pocket. The true nature of the mineral was not at first recognized; upon sending a specimen to New York, however, it was there identified.

A more thorough investigation of the region where gadolinite was first obtained, has revealed the presence of a large number of other minerals containing rare metals. The following may be mentioned:

Fergusonite; a columbate containing forty-two per cent. of yttrium oxides.

Allanite; a silicate containing from thirteen to twenty per cent. of oxide of cerium, and in addition oxides of lanthanum and yttrium.

Yttriolite; a new thorium-yttrium silicate.

Thoro-gummite; a hydrated uranium thoro-silicate.

Nivenite; a hydrated thorium-yttrium-lead uranate.

— The study of the yttrium oxides, one of the most difficult portions of the chemical field, has been pursued with great ardor and unstinted labor by a large number of able chemists. Some of them have worked for many years upon the subject. But the difficulties are very great and it seems likely that (unless some entirely new chemical agency is devised) the various elements of the series will not be thoroughly separated in the next thirty years.

— For many years, Mr. William Crookes (now Sir William) of London, who has studied with extraordinary earnestness the metals of the gadolinite and samarskite series, has employed, for *separation of the oxides*, the process known as "fractionation" — a method, speaking generally, of the limited or fractional precipitation of substances.

For *recognition of the degree of purity of a given product*, he has produced phosphorescent spectra. By this means he has recently been able to distinguish differences in compounds of these metals that have never before been recognized. Thus, five varieties of an "yttrium" compound, giving all of them the same incandescent spectrum, have been found by Crookes to yield five distinct phosphorescent spectra.

— Mr. Waldron Shapleigh has produced in the United States, specimens of salts of the rare metals such as have never before been seen. He has worked for years, upon tons of cerite and monazite, in some cases carrying on as many as 400 fractionations of a given product.

SCANDIUM; Sc; 44,12.

The word scandium is derived from the geographical name, Scandinavia.

The oxide was discovered by Nilson, in 1879, in gadolinite. It also exists in polycrase. The metal has not been satisfactorily isolated, but it probably corresponds closely with the properties expected by Mendeléeff in his predicted metal eka-boron. (See pp. 176–179, and 188.)

Many so-called salts of scandium have been produced.

YTTRIUM; Y; 89,02.

The word yttrium is derived from Ytterby, the name of a place in Sweden.

The oxide was discovered by Gadolin, in 1798, in gadolinite. It also exists in many other minerals. The pure metal has not yet been obtained.

Many so-called salts of yttrium have been produced. (See pp. 176–179.)

LANTHANUM; La; 138,64.

The word lanthanum is derived from the Greek word λανθάνω (*lanthano*) I conceal.

The oxide was discovered by Mosander, 1839–41, in gadolinite. It exists in several other minerals.

The metal has been prepared; it is white; its density is about 6.16.

Many lanthanum salts of a high degree of purity have been prepared by W. Shapleigh.

YTTERBIUM; Yt; 173,19.

The word ytterbium is derived from Ytterby, the name of a place in Sweden.

The oxide was discovered by Marignac, in 1878, in gadolinite. It exists in several other minerals. The metal has not yet been satisfactorily isolated. (See pp. 176–179.)

ALUMINIUM; Al; 27, 11.

Introduction — Distribution, preparation, properties, and compounds of Aluminium.

Data for Reference.

Density of solid aluminium 2.58 (water being the standard = 1).
Fusing point of solid aluminium about 700° C.
Aluminium was first produced as a metal by F. Wöhler, in 1828.
The word aluminium is derived from the Latin word *alumen*, alum.

Introduction.

The ancients knew the mineral substance alum, but they did not understand its composition. About 100 years ago, it was clearly recognized that alum is a double salt containing two metals, the one aluminium, the other potassium (but at that time neither was producible in a metallic form).

Aluminium is by far the most abundant of the metals. It has already been shown that about three-quarters of the terrestrial globe is composed of silicon and oxygen; about one-third of the remainder is found to be aluminium, *i. e.*, from seven to nine per cent. of the whole.

It might be supposed that the great abundance of aluminium in the earth would have lead to its early manufacture as a metal. The reason why it has been manufactured only in the last forty years is referable to the great affinity of aluminium for those elements, oxygen and silicon, with which it is ordinarily found in the earth. When Sir Humphry Davy discovered that certain inorganic substances, not previously decomposed, were compounds, and contained within them special metals, such as potassium, sodium, barium, strontium, calcium, he felt confident that another special metal exists in alum. It was reserved, however, for Wöhler in 1828 to first produce the pure elementary substance.

Distribution of Aluminium.

Aluminium exists in the earth as an oxide called alumina, Al_2O_3. It is also found as the mineral bauxite, $Al_2Fe_2O_5H_4$. It occurs also in many other minerals, such as feldspars, and the clays derived by a natural decomposition of feldspars. In Greenland, it occurs as a beautiful white mineral called cryolite, a double fluoride of aluminium and sodium, $Al_2F_6 \cdot 6NaF$.

Preparation of Aluminium.

1st — Wöhler prepared the metal by the action of metallic *potassium* upon aluminic chloride. A great step in advance was taken when Deville studied the subject. He modified Wöhler's process, using metallic *sodium* to decompose a double chloride of sodium and aluminium.

2d — Castner undertook to carry out Deville's process more cheaply * by producing *cheaper sodium.* His first and second methods have been described already under Sodium.

In the second stage of the work he prepares *the double chloride of aluminium and sodium* in retorts similar to those of gas works. The retorts are charged with blocks of a mixture containing aluminic hydroxide, common salt and charcoal. The blocks are made somewhat as bricks are. They are placed on top of some of the furnaces to dry. When dry they are charged into the retorts, and are baked so as completely to expel all water. When this has been accomplished a current of chlorine gas, from a large gas-holder, is passed into the retorts for seventy-two hours. By that time the reaction is completed, and the vapors of the double chloride are allowed to pass away through an exit pipe, whereupon they condense in solid masses having the formula $AlCl_3NaCl$.

In the third stage of the work he prepares *aluminium.* The double chloride and metallic sodium (with cryolite) are thoroughly intermingled and then placed in a reverberatory furnace. The substances react promptly, and in a few hours the liquid aluminium may be drawn from the bottom of the furnace as a silvery stream.

3d — Hall's process. This process, now conducted on a large scale at Niagara Falls, has done away with all others: by it practically all the aluminium of trade is prepared.

In outline the process is as follows: A metallic crucible provided with a thick lining of gas-carbon is employed. It forms the negative electrode. The crucible is filled with a mixture of cryolite and aluminic oxide. In the mixture is suspended the positive electrode. When a suitable electric current is transmitted through the system, heat is produced and the cryolite melts. Now the

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* An interesting account of this splendid chemical operation is given in the *Journal of the Society of Chemical Industry* for June 29th, 1889, from which we quote. The description is by Sir H. E. Roscoe.

aluminic oxide floating in the melting cryolite decomposes. Metallic aluminium gathers at the walls of the crucible and falls to the bottom. It is drawn off from time to time, and new aluminic oxide is introduced into the bath, to be in turn decomposed as described.

Uses of Metallic Aluminium.

At the present day aluminium is well known in the metallic form. In England, France, Germany, and the United States aluminium is now produced in large quantities for use in the manufacture of certain useful and ornamental articles, such as scientific instruments, opera glasses, and even table spoons. If the substance can be produced at a lower price it will undoubtedly come into much more extended use in the future. Its lightness, and its white color, not readily concealed by tarnishing, are among its chief recommendations.

Properties of Aluminium.

Aluminium is a bluish-white metal which is capable of receiving a very brilliant polish. It is sufficiently malleable to be rolled out into very thin leaves, and ductile enough to form fine wire. It is very sonorous, so that musical instruments may to advantage be made from it as well as from its alloys. It is very light in weight, being less than three times as heavy as water, whereas the other metals in common use, such as iron, copper, and the like, are from seven to nine times as heavy as water.

Aluminium forms certain valuable alloys, of which aluminium bronze is the most important. This is a combination of 90 per cent. of pure copper and 10 per cent. of aluminium. It has an elegant color, resembling gold, and it takes a high polish. Moreover it has a tensile strength equal to that of cast steel. Thus it has come into large use in the arts. (It is also worthy of note that the strength of cast iron is increased materially by blending a small amount of aluminium in it.)

Aluminium does not tarnish in the air, or when exposed to vapors containing sulphur, as some other white metals do. The metal dissolves, however, in many chemical solvents, such as hydrochloric acid, and even the caustic alkalies like sodium hydrate.

A Few Compounds Containing Aluminium.

With fluorine;	Aluminium fluoride, Al_2F_6	
With chlorine;	—— chloride, Al_2Cl_6	
With bromine;	—— bromide, Al_2Br_6	
With iodine;	—— iodide, Al_2I_6	
With oxygen;	Aluminium oxide, Al_2O_3;	Aluminium hydroxide, $Al_2O_6H_6$
With sulphur;	—— sulphide, Al_2S_3;	—— sulphate, $Al_2(SO_4)_3$
With boron;	Aluminium boride, AlB_2	
	another —— AlB_{12}	
With nitrogen;		Aluminium nitrate, $Al_2(NO_3)_6$
With phosphorus;		—— phosphate, $Al_2(PO_4)_2$
With silicon;		(many silicates)
With metals;		(many aluminates)
		(many alums)

Aluminium oxide or alumina, Al_2O_3. — This is the only oxide of aluminium known. It occurs in nature in the crystalline form in certain minerals, such as corundum, found in considerable abundance in the United States; also in the ruby, and sapphire. A less pure alumina is found, and it is used in the arts under the name of emery. All these natural minerals are hard, and when in the form of powder they may be used for polishing purposes.

Messrs. Fremy and Verneuil have produced rubies and sapphires artificially by proper treatment of compounds of aluminium in large crucibles heated by powerful gas furnaces. By such means, they have produced by a single operation as much as six pounds of rubies. As yet, the artificial gems produced are not as large as might be desired. Probably in the future, the present difficulties will be overcome.*

Aluminium hydroxide, $Al_2O_6H_6$. — This substance is produced when to a soluble salt of aluminium, ammonium hydroxide is added under favorable conditions. It is a white, gelatinous, and very bulky precipitate. It is insoluble in water, but dissolves in many chemical reagents. When the precipitate is filtered and dried, it shrivels down to a very small bulk of solid.

Aluminium sulphate, $Al_2(SO_4)_3$. — This substance is used to some extent in dyeing and calico printing. It is known as concentrated alum and sometimes as alum-cake. It is largely used in the manufacture of alum.

Alum. — The term alum is derived from a Latin word *alumen.* The ancients knew this astringent material, found in the earth, and they employed it in medicine and in dyeing. In the middle

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* *La Nature*, December 6, 1890.

ages alum was manufactured by certain processes whose principles were not well understood. At the present day, however, they are clearly comprehended. It is now recognized that the ancient alum was a double-salt now called potassio-aluminic sulphate, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

Moreover in the progress of modern chemistry it has been found that a great many substances, having certain of the general properties of alum and having its general composition, may be made by the use of slightly different materials. Thus, for the *potassium* may be substituted sodium, ammonium and even other alkali metals. On the other hand, for the *aluminium* may be substituted iron, manganese, chromium and certain other metals. Thus the term alum, originally applied to a single substance, is now applied to a *class* of substances.

Manufacture of alum. — The alum of commerce was at first potassio-aluminic alum exclusively. With the development of the illuminating gas industry, however, a new source of ammonia was discovered. The price of ammonium salts being reduced thereby, it became evident that ammonia alum could be manufactured to advantage. During the middle of the present century, ammonium alum became the alum of commerce. With the discovery of the Stassfurt potassium deposits the price of potassium compounds fell, while at the same time there arose increased demands for ammonia for cooling machines, etc. These combined circumstances led to the renewed use of potassium compounds in alum.

The manufacture of alum is now carried on somewhat as follows: Bauxite is dissolved in sulphuric acid to form aluminium sulphate. Potassium sulphate is added to the aluminium solution. The filtered liquid is then transferred to enormous casks having movable sides. The alum crystallizes and soon produces a nearly solid mass in the casks. In due time the sides of the casks may be removed, leaving a tower of alum. A hole is drilled at the bottom of the alum mass, in order to allow the mother liquor to drain away. When the alum crystals have sufficiently drained they are broken up and packed in barrels for sale.

Ammonia alum, $(NH_4)_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. This alum is often largely used in manufactures. It is prepared by dissolving aluminium sulphate and ammonium sulphate in water, and then crystallizing.

Uses of Aluminium Compounds.

First, in dyeing. — Aluminium compounds have a most striking affinity for coloring matters. If, in a liquid containing coloring matter, aluminium hydroxide is introduced, the hydrate soon combines with the coloring matter, whether the latter is animal, vegetable or mineral. The new compound settles to the bottom of the vessel as a precipitate called a lake. This property of aluminium compounds is largely utilized in dyeing. Aluminium compounds, like other mineral matters which possess this property, are called mordants. When they are applied to textile fabrics, a subsequent application of a vegetable or animal dye-stuff gives rise to a formation, on the fibres, of a distinct coloring matter. This is the principle on which the chief processes of dyeing depend.

Second, in clarifying liquids.— If aluminium hydroxide is placed in a liquid containing in suspension fine particles of a solid, the hydroxide gathers the particles of solid to itself, and the whole mass subsides, and in time the liquid becomes clear. If it is filtered, a perfectly clear liquid runs away, the solids being retained on the filter. This property of aluminium compounds is now largely utilized in the arts. It is often employed for the purification of city sewage.

Third, in the manufacture of bricks, earthenware, porcelain and glass.—Minerals containing aluminium are largely employed in the manufacture of these most useful materials.

The peculiar power of clay, when mixed with certain other substances and baked, of producing a coherent, fire-proof substance similar to stone, has been utilized from early times. The making of bricks and tiles in Egypt and other parts of the ancient East was one of the most important of the early arts. Up to the present day no better non-combustible material for building purposes has ever been devised, and the manufacture of bricks and tiles in their commoner or more ornamental forms is now one of the most important and interesting of arts. The manufacture of pottery of the coarser kinds was a step associated with the manufacture of bricks and tiles.

Bricks consist essentially of baked clay, and the clay is essentially aluminium silicate. Most clay, however, contains intermixtures of sand and other mineral substances. Often these impurities are such as are unfavorable to the quality of the bricks produced.

In the preparation of clay for the manufacture of bricks, pebbles should be removed. If these are of limestone, the burning decomposes them, producing quicklime, which is subsequently liable to injure the manufactured brick. It is said that small quantities of pyrites, if thoroughly distributed, are somewhat favorable. The iron seems to combine with silica and so form a compound, that helps to bind the parts of the brick together.

The manufacture of bricks is, in brief, as follows :

The clay having been dug from the bank, is put through a mill, for the purpose of making the material uniform, as well as with a view to separation of any hard minerals that occur in it. From the mill, the properly prepared clay, streams out as a long, rectangular prism. A system of wires falling upon this prism, cuts it up into fragments of the proper size of a brick. In some cases substances are added to the clay, as chalk and charcoal.

Bricks are manufactured by a *dry process* as well as by a wet process. Those made by the wet process are dried either in the sun or in ovens before they are sent to the kilns. In the dry process, the clay is submitted, in a machine, to very great pressure so as to form individual bricks. These, after loading upon cars, are carried into a drying house, heated by steam.

The kilns are ordinarily constructed of fire brick. In the old process, fires being kindled at the lower part of the kiln, the gaseous products of combustion streamed *upward* through the bricks, baking them thoroughly. In the new process, the hot gases are produced in a separate furnace. They are then conveyed to the top of the kiln and drawn *downward* through the bricks piled within it.

Bricks of various grades are employed for building purposes, even certain imperfect ones, such as have warped out of shape, being now used to some extent.

Fire brick is a particularly refractory variety used for lining furnaces, and in places where they must withstand high temperatures.

Of late bricks have also been made for use in street pavements.

Porcelain is a fine kind of ware distinguished from *earthenware or faience* in the fact that porcelain is translucent while faience is not. In porcelain also the finer kinds of clay are employed.

The better kinds of *glass* are made from sand, or some form of silicic oxide (SiO_2) together with potassium or sodium compounds, while the commoner bottle-glass involves the addition of materials containing aluminium compounds.

GALLIUM; Ga; 69, 91.

Data for Reference.

Density of solid gallium 5.96 (water being the standard = 1).

Fusing point of solid gallium 30.15°C.

Boiling point of gallium unknown.

Gallium was discovered by Lecocq de Boisbaudran in 1875,

The word gallium is derived from *Gallia*, the Latin name for Gaul.

A very interesting fact about gallium is the circumstance that when Mendeléeff arranged his periodic table he called attention to certain spaces left vacant for metals to be hereafter discovered. Among others he gave the provisional names of three: eka-boron, eka-silicon, and eka-aluminium. Now gallium, upon its discovery, was found to correspond closely in properties to those Mendeléeff assigned to eka-aluminium. Mendeléeff said that this unknown metal should have an atomic weight of about 68, a specific gravity of about 6, and an atomic volume of about 11 5, Gallium has been found to yield on these points the numbers 69, 5 9, and 11.8, respectively. (See also Germanium and Scandium.)

Gallium is an exceedingly rare metal. It is found in minute quantities in certain varieties of zinc blende, ZnS.

The rarity of gallium is shown from the fact that one of the blendes richest in this rare metal contains only sixteen pounds of gallium in a million pounds of blende. The discoverer of gallium exhibited at the Paris Exposition of 1878 about two ounces of the metal. In order to obtain this amount he had worked upon above five thousand pounds of blende.

Gallium may be prepared by electrolysis of certain of its compounds.

Gallium in the metallic form is bluish-white in color. One of its striking properties is that of fusing at about the temperature of the hand.

Many compounds of gallium have been prepared. They correspond, in general, to those of aluminium. Thus, gallium forms a chloride, Ga_2Cl_6; a corresponding oxide, Ga_2O_3; and a double sulphate, which may be called ammonio-gallic alum, since it crystallizes in forms allied to the cube, as do ordinary alums, and it also has a formula corresponding to alums, $(NH_4)_2SO_4 \cdot Ga_2(SO_4)_3 \cdot 24H_2O$.

At present gallium has no uses in the arts.

INDIUM; In; 113, 85.

Data for Reference.

Density of solid indium 7.42 (water being the standard = 1),
Fusing point of solid indium 176° C.
Liquid indium boils at a red heat.
Indium was discovered by Reich and Richter in 1863.
The word indium is derived from a Latin word, *indicum*, indigo.

Indium is an exceedingly rare metal It is found in certain zinc blendes in so small proportion as one part of indium to one thousand of blende.

Indium is a white metal, malleable, and softer than lead.

The characteristic feature of indium and its compounds is the power of producing dark blue light under the influence of heat. It is this property that enables indium to be detected by the spectroscope. No other means at present known would have led to the discovery of this element.

Neither indium nor its compounds have at present any commercial uses.

Many compounds of indium have been prepared. They correspond, in general, to those of aluminium. Thus, indium forms three chlorides, $InCl$, $InCl_2$, In_2Cl_6; two oxides, InO, In_2O_3; an ammonio-indium alum, $(NH_4)_2SO_4 \cdot In_2(SO_4)_3 \cdot 24H_2O$.

THALLIUM; Tl; 204, 15.

Data for Reference.

Density of solid thallium, 11.8 (water being the standard = 1).
Fusing point of solid thallium, 293.9° C.
Boiling point of liquid thallium, unknown.
Thallium was discovered by William Crookes in 1861.
The word thallium is derived from a Greek word, θαλλὸς (*thallos*), a green twig.

Thallium was discovered by William Crookes by spectroscopic examination of a certain residual product obtained from a sulphuric acid works in Germany.

It has lately been found to exist in a large quantity in a rare mineral, since named crookesite. Crookesite contains copper, silver, selenium, and seventy per cent. of thallium.

The metal is usually prepared from the flue dust of sulphuric acid works employing pyrites containing traces of thallium.

The metal thallium may be prepared by electrolysis, and by other methods.

The metal thallium somewhat resembles lead in appearance.

The most notable characteristic of thallium is the beautiful green flame color it affords when highly heated.

Many compounds of thallium have been prepared.

Thus, thallium forms two chlorides, $TlCl$, $TlCl_3$; two oxides, Tl_2O, Tl_2O_3; a sulphate, Tl_2SO_4; a nitrate, $TlNO_3$.

Sir William Crookes, eminent English chemist.

BOOK IV. — FOURTH PERIODIC GROUP.

1st Section. — TITANIUM, ZIRCONIUM, CERIUM, THORIUM.

2d Section. — GERMANIUM, TIN, LEAD.

General Comments on the Group.

None of the members of this group are very abundant — thorium and germanium are exceedingly rare.

The members of the first section form compounds after the general formula, M_2O_3 (the oxides of this type being basic) and MO_2 (the oxides of this type being feebly acid).

The members of the second section form compounds after the general formula, MO (the oxides of this type being basic), and MO_2 (the oxides of this type being both acidic and basic).

TITANIUM; Ti; 48, 15.

Data for Reference.

Density of titanium, 3.59 (water being the standard = 1).

The metal has not been fused.

A titanium compound was announced by Gregor in 1791; substantiated and named by Klaproth in 1795; the element isolated by Berzelius in 1824.

The word titanium is derived from the name of the mythical deity of the ancients, Titan.

The metal titanium exists in the mineral rutile as a dioxide, TiO_2. It also occurs in combination with iron in the mineral ilmenite, also called titanic iron, $Fe_2Ti_2O_3$. It is present in several rare minerals, also.

The metal may be prepared by heating certain of its compounds with sodium or potassium.

A Few Compounds Containing Titanium.

With chlorine;	Titanium dichloride,	$TiCl_2$		
	——— tetrachloride,	$TiCl_4$		
With oxygen;	Titanium dioxide,	TiO_2;	Titanic acid,	H_2TiO_3?
	——— sesquioxide,	Ti_2O_3,	Metatitanic acid,	H_4TiO_4?
With nitrogen;	Titanium nitrides,	Ti_5N_6		
	"	Ti_3N_4		
	"	TiN_2		
With metals;			Potassium titanate,	K_2TiO_3
			Calcium titanate,	$CaTiO_3$

Titanium exists in many iron ores. In the operation of the blast furnace some of the titanium goes with the cast-iron; some of it escapes in the slag; another portion, however, often forms a special and peculiar compound which gathers in a mass distinct by itself, cyano-nitride of titanium, $TiC_2N_2 + 3Ti_3N_2$. It is formed by the union of the titanium of the ore, the carbon of the fuel, and the nitrogen of the blast-air, all acting at a very high temperature.

ZIRCONIUM; Zr; 90,40.

Data for Reference.

Density of solid zirconium, 4.15 (water being the standard = 1).

Fusing point of solid zirconium is above 950° C.

A zirconium compound was recognized in zircon by Klaproth, in 1789; in 1824 Berzelius isolated the element.

The word zirconium is derived from the name of the mineral, zircon, in which it was first observed.

The metal zirconium is contained in the mineral called zircon; also in that called hyacinth. Both are silicates of zirconium, $ZrSiO_4$.

The metal may be produced by heating certain of its compounds with potassium, or with sodium, or with magnesium. It then appears as a grayish crystalline solid or as an amorphous powder.

A Few Compounds of Zirconium.

With chlorine;	Zirconium chloride,	$ZrCl_4$		
With oxygen;	Zirconium oxide,	ZrO_2		
With sulphur;			Zirconium sulphate,	$Zr(SO_4)_2$
With nitrogen;			Zirconium nitrate,	$Zr(NO_3)_4$
With metals;			(many zirconates)	
			Sodium zirconate,	Na_2ZrO_3

CERIUM; Ce; 140.2.

Data for Reference.

Density of solid cerium 6.6—6.7 (water being the standard = 1).

Fusing point of solid cerium is between 450° C. and 950° C.

In 1803 Klaproth announced his discovery of a new substance, probably an oxide of a new metal, cerium. In 1826 Mosander obtained a metal from the compound. (But there is doubt as to its purity.)

The word cerium is derived from the name of an asteroid, Ceres, discovered a short time before the metal was recognized.

Cerium is a relatively rare element, yet it is widely diffused. It exists in moderate quantities in several of the Swedish minerals that contain members of the yttrium group of rare elements. Yet in the mineral cerite, cerium silicate, cerium oxide, Ce_2O_3, exists to the extent of 56%. (See pp. 176–179.)

Cerium, as a metal, in somewhat impure form, has been produced by electrolysis of cerium chloride.

Certain cerium compounds have a limited application in medicine.

A Few Compounds Containing Cerium.

With fluorine;	Cerous fluoride,	CeF_3		
	Ceric ———	CeF_4		
With chlorine;	Cerous chloride,	$CeCl_3$		
With bromine;	——— bromide,	$CeBr_3$		
With iodine;	——— iodide,	CeI_3		
With oxygen;	Cerous oxide,	Ce_2O_3		
	——— dioxide.	CeO_2		
	——— peroxide,	CeO_3		
With sulphur;	——— sulphide,	CeS_3;	Cerous sulphate,	$Ce_2(SO_4)_3$
			Ceric ———	$Ce(SO_4)_2$
With nitrogen;			Cerous nitrate,	$Ce(NO_3)_3$
With phosphorus;			——— phosphate	$CePO_4$
With carbon;	Cerium carbide,	CeC_6;	Cerous carbonate,	$Ce_2(CO_3)_3$
With silicon;	——— silicide,	Ce_2Si_3		

THORIUM; Th; 232, 63.

Data for Reference.

Density of solid thorium, about 11 (water being the standard = 1).
Fusing point of solid thorium unknown (it is certainly very high).
Thorium was discovered by Jons Jakob Berzelius in 1828.
The word thorium is derived from the name of a Norse deity, Thor.

Thorium is a relatively rare element, yet it exists in a considerable number of the minerals (like gadolinite and samarskite) that contain members of the rare yttrium group of metals. Yet the rare mineral orangite contains about 74% of thorium oxide, ThO_2. The most abundant mineral containing thorium compounds is monazite, a mixed phosphate containing from 1% to 15% of the oxide.

Thorium has been produced by heating certain compounds of it with potassium or with sodium.

The use of compounds of thorium in the preparation of the mantle for the Welsbach burner has given them a new and very great commercial importance.

A Few Compounds Containing Thorium.

With hydrogen;	Thorium hydride,	ThH_2		
With fluorine;	—— fluoride,	ThF_4		
With chlorine:	—— chloride,	$ThCl_4$		
With bromine;	—— bromide,	$ThBr_4$		
With iodine;	—— iodide,	ThI_4		
With oxygen;	Thorium oxide,	ThO_2;	Thorium hydroxide,	ThO_4H_4
With sulphur;	—— sulphide,	ThS_2	—— sulphate,	$Th(SO_4)_2$
With nitrogen;			Thorium nitrate,	$Th(NO_3)_4$

The Welsbach Burner.

Carl Auer von Welsbach, a distinguished Viennese chemist, observed that when certain oxides of the rare metals were heated, in the non-luminous flame of the Bunsen burner, they emitted far more light than the amount of gas consumed would afford when burned from ordinary illuminating tips. Following this suggestion, he invented the Welsbach incandescent burner.

His invention, which came before the public about 1868, is at present used all over the civilized world. It involves the following operations: A woven cotton tube is impregnated with nitrates of certain rare metals — of thorium, of cerium, and of neodymium, and perhaps others. When this tube is suspended over a Bunsen flame, the cotton burns away, leaving a skeleton of oxides, which glow with an intensely white light.

The invention has been enormously profitable to some of the companies interested in it. This circumstance has stimulated study of the whole subject, and as a result the mantles have been steadily improved.

The great number of mantles used has created a previously unheard of demand for thorium compounds, and thence for the thorium minerals (chiefly for monazite).

Monazite exists as workable deposits in the form of sands that have been concentrated by some natural process, like erosion, or secular movement of loose material, under the influence of streams, or of the waves on sea beaches.

Monazite sands are found in the United States chiefly in North Carolina. The deposits are washed in sluice boxes, the lighter sands being washed away, and those richest in monazite being left. In Brazil, extensive deposits occur on beaches along the sea coast; the sea waves have accomplished a concentration of the sands. Indeed, the cheapness of the Brazilian monazite has led to an almost entire cessation of the commercial working of the North Carolina field.*

Following are the results of analyses of typical specimens of monazite, made by Prof. S. L. Penfield of Yale University:

Monazite.

	From Portland, Conn.	From Burke Co., N. C.	From Amelia Co., Va.	From Alexander Co., N. C.
	1	2	3	4
P_2O_5	28·18	29·28	26·12	29·32
Ce_2O_3	33·54	31·38	29·89	37·26
La_2O_3	28·33	30·88	26·66	31·60
ThO_2	8·25	6·49	14·23	1·48
SiO_2	1·67	1·40	2·85	0·32
H_2O	0·37	0·20	0·67	0·17
	100·34	99·63	100·42	100·15

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* The following references give accounts of many matters incident to monazite, and to the Welsbach mantle:

Sci. Am. Supp., Jan. 11, 1896, p. 16,704; Oct. 28, 1897, p. 18, 196.

The Mineral Industry, 2: 558; 3: 455; 4: 545; 5: 482; 6: 487.

GERMANIUM; Ge; 72, 48.

Data for Reference.

Density of solid germanium, 5.47 (water being the standard = 1).
Fusing point of solid germanium, about 900° C.
Germanium was discovered by Clemens Winkler, in 1885.
The name germanium is derived from *Germania*, the Latin name for Germany.

Germanium exists in an exceedingly rare mineral, argyrodite, which is a double sulphide of silver and germanium (about 6.9 per cent. of germanium) but which contains in addition minute quantities of iron, mercury, and zinc. Germanium has recently been detected in certain varieties of euxenite. (See page 178.)

A most interesting fact with respect to germanium is that it was found to be practically identical with a previously unknown element, predicted as possible by Mendeléeff, and by him provisionally named ekasilicium.

A Few Compounds Containing Germanium.

With fluorine;	Germanium fluoride,	GeF_4
With chlorine;	——— chloride,	$GeCl_4$
	——— chloroform,	$GeHCl_3$
With bromine;	——— bromide,	$GeBr_4$
With iodine;	——— iodide,	GeI_4
With oxygen;	Germanium monoxide,	GeO
	——— dioxide,	GeO_2
With sulphur;	——— monosulphide,	GeS
	——— disulphide,	GeS_2
With carbon;		
	Germanium ethide,	$Ge(C_2H_5)_4$

TIN; Sn; 119,05.

Introduction — Distribution, preparation, properties, and compounds of tin.

Data for Reference.

Density of solid tin, 7.29 (water being the standard = 1).
Fusing point of solid tin, 232.7° C.
Boiling point of liquid tin is between 1450° and 1600° C.
Tin was known to the ancients (and apparently from very early times).
The symbol Sn is an abridgement of the Latin word, *stannum*, tin.

Introduction.

Tin was known by the ancients, but they sometimes confused metallic lead with metallic tin, thinking them only different varieties of the same metal.

It seems tolerably certain that the Phœnicians brought tin ore or metallic tin from that portion of England known as Cornwall.

Distribution of Tin.

The chief ore of tin is an oxide called cassiterite or tinstone, a tolerably pure stannic oxide, SnO_2.

The Cornish mines are still among the most important sources of the metal; but ores of tin are obtained from Banca, and perhaps other islands near the Malay Peninsula. From certain portions of Australia, also, a considerable quantity of tin is obtained.

Preparation of Tin.

There are many different metals which, upon introduction into a solution containing stannous chloride, $SnCl_2$, liberate the tin as spongy masses; zinc does this promptly.

Metallurgic Extraction of Tin.

The ore, as excavated, is broken into small portions and then picked by hand, or washed by machine, for the purpose of excluding worthless material.

The selected ore is roasted in a rotating furnace. The rotation accomplishes a transfer of the ore toward hotter and hotter portions of the furnace. Thus, roasting proceeds gradually, and certain injurious components of the ore — sulphur, arsenic and the like — are vaporized. They are carried forward into flues where the arsenic, at any rate, condenses. Sometimes more than one roasting and more than one washing are practised.

Fig. 69. Surface works of Botallack tin mine, Cornwall, England. (The shafts are 1,050 feet deep; the horizontal levels stretch 1,200 feet under the sea.)

The ore is next smelted in presence of fine coal and lime. The carbon withdraws oxygen from the tin, while the lime combines with certain impurities of the ore. The melted tin gathers beneath the slag.

The metal is subjected to further purification if necessary.

Commercial tin sometimes contains small quantities of arsenic, copper, and yet other impurities.

Tin is a very useful metal in the arts. Its chief uses are for coating other metals; in the production of alloys; and in the processes of coloring textile fabrics.

The coating of metals with tin — The so-called tin plate used for roofing and the so-called sheet tin used for tin ware, is iron coated with tin.

The material is produced somewhat as follows: Tin is melted in a large kettle. The upper surface of the metal is protected from oxidation by a layer of palm oil, or resin, or sal ammoniac, distributed on it. The iron to be coated is cleaned by dipping it in acid, and then, it may be, in some kind of melted fat. The acid removes oxide from the surface. The melted fat prevents access of air, which would oxidize the metal. Next, the sheet is dipped in the tank of melted tin, whereupon the tin adheres to the surface. For the better qualities of plate more than one dip may be practised. For inferior qualities of plate an alloy of tin and lead is sometimes used.

Copper vessels are often tinned in accordance with the same general treatment.

Tin in alloys. — Tin is used to a considerable extent in alloys with copper and zinc, producing with them that alloy called bronze. The metal, when cast, fills well the crevices of the mold. It is capable of a high polish.

It has at first a yellow color like brass; but this, in time, by exposure to the atmosphere, becomes tarnished so that the metal takes a dark rich color. The thin layer of tarnish protects the metal underneath from further oxidation, so that bronze articles are very enduring. Ornamental bronzes are usually *colored artificially* so as to produce the particular shade desired.

Tin compounds in textile coloring. — Tin compounds are very valuable as mordants in the dyeing of cotton, and woolen goods, morocco leather, etc. Their advantage is twofold: *First*, with certain dye stuffs, especially cochineal, brilliant and lasting red

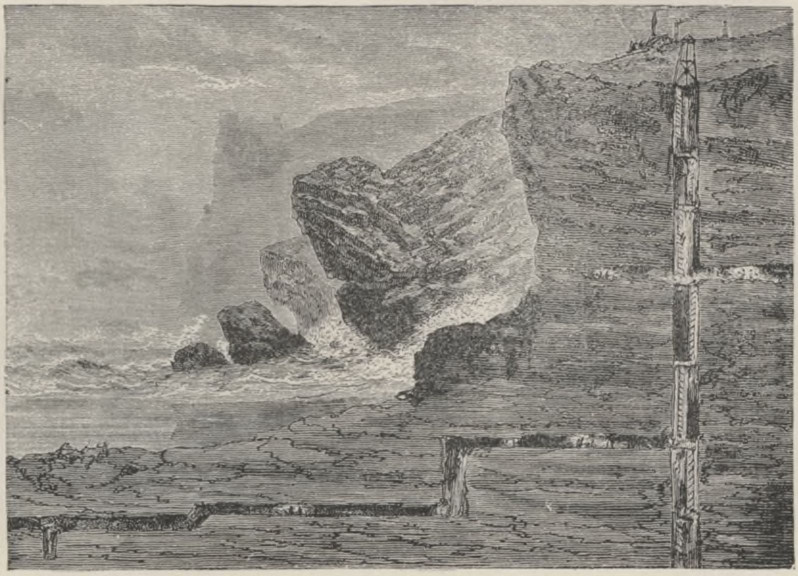

Fig. 70. Subterranean shafts and galleries of Botallack tin mine, Cornwall, England.

colors are formed; *second*, tin salts have the remarkable property of increasing the affinity of vegetable and other fibres for coloring matters, so that certain proportions of tin compounds introduced into coloring substances increase the intensity, brilliancy, and permanence of the shade produced.

Tin has a fine white color, somewhat like that of silver. When a mass of it is bent, it produces a peculiar sound called the "tin cry."

It does not readily oxidize on exposure to the air. When highly heated, it burns, forming a white oxide, stannic oxide, SnO_2, in the form of powder.

Tin dissolves easily in hydrochloric acid, forming stannous chloride, $SnCl_2$.

Tin is attacked by nitric acid, but an *insoluble* compound is produced, called metastannic acid.

Tin is sometimes classed as a non-metal.

Tin forms, with non-metals, two distinct series of compounds, the *stannous* and the *stannic;* with metals the stannic oxide forms *stannates*.

A Few Compounds Containing Tin.

With fluorine;	Stannous fluoride,	SnF_2		
With chlorine;	Stannous chloride,	$SnCl_2$		
	Stannic ——	$SnCl_4$		
With bromine;	Stannous bromide	$SnBr_2$		
	Stannic ——	$SnBr_4$		
	Stannic bromhydric acid,	H_2SnBr_6;	Barium stannibromide,	$BaSnBr_6$
With iodine;	Stannous iodide,	SnI_2		
	Stannic ——	SnI_4		
With oxygen;	Stannous oxide,	SnO		
	Tin sesquioxide,	Sn_2O_3		
	Stannic oxide,	SnO_2;	Metastannic acid,	$H_{10}Sn_5O_{15}$
			Sodium stannate,	Na_2SnO_3
			Potassium ——	K_2SnO_3
			Barium ——	$BaSnO_3$
With sulphur;	Stannous sulphide,	SnS;	Sulphostannic acid,	H_2SnS_3
	Stannic ——	SnS_2;	Sodium sulpho stannate,	Na_2SnS_3
			Potassium ——	K_2SnS_3
			Stannous sulphate,	$SnSO_4$
With selenium;	Stannous selenide,	$SnSe$		
	Stannic ——	$SnSe_2$		
With tellurium;	Stannous telluride,	$SnTe$		
With nitrogen;			Stannous nitrate,	$Sn(NO_3)_2$
With phosphorus;	Tin phosphide,	SnP		
With carbon;	(Many organo-tin compounds.)			
	Stannic methide,	$Sn(CH_3)_4$		
	Stannous ethide,	$Sn(C_2H_5)_2$		
	Stannic ——	$Sn(C_2H_5)_4$		

Stannous chloride. This substance is produced by dissolving tin in hydrochloric acid. The chemical change is produced as follows :

$$Sn + 2HCl = SnCl_2 + H_2$$

When the solution produced becomes concentrated by evaporation or otherwise, crystals having the formula $SnCl_2 \cdot 2H_2O$ are formed. They are largely used in the arts under the name of tin crystals. Their chief employment is in calico printing and the dyeing of textile fabrics.

LEAD; Pb; 206, 92.

Introduction.— Distribution, preparation, properties, uses, and compounds of lead (especially white lead).

Data for Reference.

Density of solid lead, 11.25 — 11.39 (water being the standard = 1).
Fusing point of solid lead, 326.2° C. (by air thermometer).
Boiling point of liquid lead, 1450° — 1600° C.
Lead was known by the ancients, and apparently in very early times.
The derivation of the name lead is uncertain.
The symbol, Pb, is an abridgement of the Latin word *plumbum*, lead.

Introduction.

The ancients evidently knew the metal lead, although they may have confused it to some extent with the similar metal tin. The ancient Romans, however, employed lead to a considerable extent. They were well aware, for instance, that although a convenient substance for the construction of water pipes, its use is attended with danger of poisoning.

Distribution of Lead.

1 — Lead exists in the earth in a very large number of different compounds. The chief ore is undoubtedly galena, lead sulphide, PbS. This brilliant mineral, characterized by distinct cubical fracture, is easily recognized. Moreover, it is widely diffused. It is found in Germany, in England, in the United States, and in many other parts of the world.

In the United States large quantities of metallic lead are produced from galena.

2 — Another important ore of lead is the mineral called cerussite, lead carbonate, $PbCO_3$.

It is worked in the United States for lead (and incidentally for the silver contained in it).

3 — Many other compounds of lead are found in the earth, but generally in small and unimportant deposits.

Preparation of Lead.

The production of metallic lead from one of its compounds may be easily accomplished by any one of the five general methods described on pp. 8 and 9. Indeed lead is often spoken of as one of the *easily-reducible* metals.

As an illustration of method 3, the following statement may be presented: an aqueous solution of lead, easily liberates the metal, as brilliant crystalline flakes, when a piece of zinc is introduced.

Metallurgical Extraction of Lead from Galena.

1 — The process of smelting galena is conducted in a reverberatory furnace; it involves two stages.

In the *first stage*, the ore being moderately heated and a current of air passing over it, a certain amount of oxidation takes place. Some galena is changed from plumbic sulphide to plumbic sulphate. Thus,

$$PbS + 2O_2 = PbSO_4.$$

Again some galena is changed to lead oxide:

$$2PbS + 3O_2 = 2PbO + 2SO_2.$$

After this preliminary roasting comes the *second stage*: The temperature is raised, whereupon the oxide and the sulphate react with another portion of sulphide yielding metallic lead as follows:

$$2PbS + 2PbO + PbSO_4 = 5Pb + 3SO_2.$$

The sulphur dioxide escapes as a gas.

2 — Another method sometimes employed in Germany is more simple in its chemical nature. It consists in melting the sulphide with fragments of cast iron. The iron has a strong affinity for sulphur. In the furnace, it withdraws sulphur from the lead, leaving the latter in the metallic form.

Extraction of Lead from Silver-Lead Ores.

The following is a general outline of the process of smelting silver-lead ores in the United States:

It is conducted in a vertical furnace (blast-furnace).

— The ores are finely pulverized and thoroughly mingled so as to afford a uniform product. Carefully selected samples are then tested by the works chemist. From this test it is easy to determine the kinds and quantities of the fluxes demanded in the particular case.

— The proper fluxes are mixed with the ore, and fuel is added (coke or charcoal), to the extent of about one-seventh of the charge. The mixture is then shovelled into the top of the smelting furnace (supposed to be in full operation, for it must run night and day). Combustion and chemical action at once set in. Metallic lead is produced throughout the charge. It falls through the heated materials in the furnace like a fine rain; and coming in contact with particles of silver, it alloys with even the most minute portions, carrying them in the liquid drops to the bottom of the furnace.

— The furnace is provided with two tap-holes, the one lower than the other. Every few minutes the upper one is opened, and the melted fluxes stream out in a form called slag. This is received in little iron barrows shaped like an inverted cone. When the slag has cooled sufficiently it is dumped in one portion of the yard. It is generally assayed in order that a watch may be kept upon the running of the furnace. Often certain portions of metal form at the apex of the cone of slag. They are broken off and returned to the furnace.

The other tap hole is opened at rarer intervals. Being lower, it furnishes lead (containing the silver, and of course any gold that may be in the ore). This lead bullion, as it is called, is run into lead bars or ingots, called bricks. The bricks are sent to the cupel furnace where the lead and silver are separated.

Extraction of Silver from Lead.

It is a remarkable fact that nearly all lead contains silver. Even salts of lead which have been made from tolerably pure metal still contain minute traces of silver. All ores of lead contain silver, though in varying quantities. Ingenious methods have been devised for separating the lead and silver.

1.— One of the best known is that called *Pattinson's*. This method is really a process of crystallization, not very different from that employed in crystallizing salts from their water solution.

— The alloy of lead, containing some silver, is heated in a kettle. This kettle is usually the central one of a series extending on either side. After the first charge of metal has become liquid, it is allowed to cool to a certain temperature. Thereupon, solidification commences very gradually; that is, minute crystals of comparatively pure lead begin to form.

— After this operation has gone on to a certain degree, the crystals so formed are withdrawn by means of skimmers. These crystals are transferred to an adjoining kettle. The principal portion of the silver now remains, associated with some lead that has not crystallized. This enriched lead is transferred to the kettle on the other side of the central one. A new portion of lead is now placed in the central one. It is melted; it is crystallized; it is skimmed as before. — The operation is repeated again and again, not only on the central kettle, but on the side ones. Thus purer and purer lead is carried to one side, and lead containing more and more silver is carried to the other side. Finally, when the lead on this side becomes sufficiently rich in silver, it is subjected to the process of cupellation.

2.— Another process for desilvering lead is that called *Parkes's process*. In this process, lead containing silver is melted, and then a certain portion of zinc is added. Now, upon cooling, the alloy of zinc and silver comes to the surface. This alloy is skimmed off, and afterwards purified from zinc, whereupon the silver is obtained.

Uses of Metallic Lead.

Metallic lead has a great variety of uses in the arts.

In the form of sheet lead, it is used to some extent for roofing. Its great weight, however, is an objectionable quality; strong timbers are requisite to support it. On this account it is now replaced by tinned iron.

The usefulness of lead for roofing is diminished also by its tendency to wrinkle. Under the heat of the sun a sheet of lead expands and forms wrinkles. These only partly disappear by subsequent cooling. In this way, little by little, lead creeps up into folds which subsequently crack. Thus leaks are created.

—The objection to the use of lead pipe is the tendency of the lead to dissolve, to some extent, in water. Thus drinking water may be rendered poisonous. As a matter of fact, however, vast quantities of lead water-pipes are used without serious results.

The danger is overcome if the water, which has been resting in the pipes for a few hours, is allowed to run away. Fresh water may then be drawn without allowing time for lead to enter into solution.

— Owing to its great weight, lead is employed as ballast for small sailing vessels. Yachts are often constructed with a hollow iron keel. Then melted lead is poured into the space thus afforded. Upon hardening, it is in condition to serve its purpose.

— Some of the properties of lead fit the metal for a multitude of smaller uses. Its softness makes it practicable for use as *washers* where two metallic surfaces are to be temporarily held together.

—Lead is much used in certain alloys. Type-metal affords an excellent example. It is composed of lead and antimony.

A Few Compounds of Lead.

With fluorine;	Lead fluoride,	PbF_2		
With chlorine;	—— chloride,	$PbCl_2$;	Lead chlorite,	$Pb(ClO_2)_2$
	—— tetrachloride,	$PbCl_4$		
	—— chlorofluoride,	$PbCl_2 \cdot PbF_2$		
With bromine;	—— bromide,	$PbBr_2$		
	—— bromochloride,	$PbBrCl$		
With iodine;	—— iodide,	PbI_2		
	—— iodochloride,	$PbCl_2 \cdot PbI_2$		
	—— ——	$2PbCl_2 \cdot PbI_2$		
	—— iodobromide,	$PbBr_2 \cdot PbI_2$		
	—— ——	$3PbBr_2 \cdot PbI_2$		
	—— ——	$6PbBr_2 \cdot PbI_2$		
With oxygen;	Lead suboxide,	Pb_2O;	Basic lead hydroxide,	$Pb_2O(O_2H_2)$
	—— monoxide (litharge),	PbO;	Lead hydroxide,	PbO_2H_2
	—— sesquioxide,	Pb_2O_3;	Plumbic acid,	H_2PbO_3
	Red lead, or minium,	Pb_3O_4		
	Lead dioxide (brown),	PbO_2		
	Lead oxychloride,	$PbCl_2 \cdot PbO$		
	—— ——	$PbCl_2 \cdot 3PbO$		
	—— ——	$PbCl_2 \cdot 7PbO$		
	—— oxybromides,			
	—— oxyiodides,			
With sulphur;	Tetra lead sulphide,	Pb_4S		
	Lead subsulphide,	Pb_2S		
	—— monosulphide,	PbS		
	—— sulphochloride,	$3PbS \cdot PbCl_2$;	Lead sulphate,	$PbSO_4$
			—— sulphite,	$PbSO_3$
With selenium;	Lead selenide,	$PbSe$		
With boron;	Lead borofluoride,	$PbF_2 \cdot 2BF_3$		
With nitrogen;			Lead nitrite,	$Pb(NO_2)_2$
			—— nitrate,	$Pb(NO_3)_2$
With phosphorus;			—— phosphate,	$Pb_3(PO_4)_2$
With carbon;			Lead carbonate,	$PbCO_3$
			—— thiocarbonate,	$PbCS_3$
			(several forms of white lead)	
	Lead cyanide,	$Pb(CN)$;	Lead cyanate,	$PbO_2(CN)_2$
			—— sulphocyanate,	$PbS_2(CN)_2$
			—— selenocyanate,	$PbSe_2(CN)_2$
			Potassium plumbate,	K_2PbO_3

Lead chloride, $PbCl_2$, is produced upon addition of hydrochloric acid or certain soluble chlorides to solutions of certain lead salts, e. g., lead nitrate. It is a white crystalline product readily soluble in boiling water.

Lead iodide, PbI_2, is analogous in its preparation and properties to lead chloride, only the iodide possesses a beautiful yellow color.

Lead monoxide, PbO, is formed when lead is heated in the air. A true combustion takes place, the oxygen of the air uniting with the metallic lead. Under certain circumstances, as in the process of cupellation, this oxidation is attended with manifest production of heat. The oxide, under the name of litharge, is used to some extent in the arts.

Red lead, or minium, Pb_3O_4, is produced by heating litharge in a suitable vessel in a furnace, with access of air. Oxygen is absorbed and the substance changes in color to the well known bright red shade. Undoubtedly commercial red lead contains more oxygen than the oxide specified above. It may be a mixture of several oxides.

Lead nitrate, $Pb(NO_3)_2$, is produced by the action of nitric acid upon metallic lead, upon oxide of lead, and upon certain other lead compounds. It is a white salt, freely soluble in water. It is con-

Fig. 71. Section of works for producing white lead by the Dutch process.

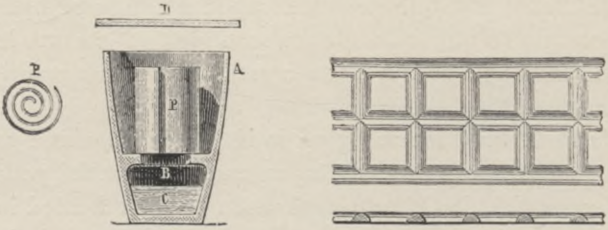

Fig. 72. Diagrams explaining the adjustment of crucibles and lead plates used in the Dutch white lead process.

siderably used in the arts. When strongly heated in a closed glass tube. it gives off brown fumes of nitrogen tetroxide, N_2O_4, or NO_2.

Lead carbonate, $PbCO_3$, is produced by adding an alkaline carbonate to a soluble salt of lead. It appears as a white precipitate.

White lead. — White lead as used in commerce is a mixture of linseed oil and hydroplumbic carbonate, or a mixture of hydroplumbic carbonates.

Probably at least four such carbonates are producible:

$$5PbCO_3 \cdot PbO_2H_2$$
$$3PbCO_3 \cdot PbO_2H_2$$
$$5PbCO_3 \cdot 3PbO_2H_2$$
$$2PbCO_3 \cdot PbO_2H_2$$

Which compound, or mixture of compounds, is present in a given sample must depend upon the conditions under which it was produced.

The salt of lead may be produced by at least three different processes:

1 — *The Dutch process.* — This is the process generally employed. Wheels or spirals of metallic lead are placed in earthenware jars containing at the bottom a small amount of vinegar. The jars are placed in orderly rows on a suitable floor and then are covered entirely with spent tan bark or other appropriate matter capable of fermentation. After a while, the bark begins to decompose and fermentation sets in. As a result, heat is produced, and carbon dioxide is liberated by the decomposition of the bark. The heat volatilizes acetic acid from the vinegar. This acid attacks the lead, forming lead acetate. Then the carbon dioxide acting upon the lead acetate, expels the acetic acid and produces lead carbonate or hydrocarbonate. The active acid so liberated may attack more lead and the whole process detailed may go on until the wheels of lead are almost entirely altered into the salt.

The operation requires three or four weeks; at the end of this time the bark is removed, the material in the jars is taken out, and everything made ready for a repetition of the undertaking. If any lead is left uncorroded, it is melted and cast into wheels for succeeding treatment.

2 — *The French precipitation process.* — Carbon dioxide is passed into an aqueous solution of a lead acetate. The white salt is precipitated.

3 — *The Brown electrolytic process.* — This process is conducted in three stages:

— Sodium nitrate is electrolyzed, in a cell divided by a porous partition, using a lead bar as the positive electrode. Sodium hydroxide and lead nitrate are formed.

— In another tank the sodium hydroxide and the lead nitrate are mixed in proper proportions to form lead hydroxide and sodium nitrate. (The latter is carried back, to be again electrolyzed with the lead anode.)

— The lead hydroxide, PbO_2H_2, is brought in contact with a solution of sodium hydrocarbonate, $HNaCO_3$. As a result, white lead is formed.

It is stated that the product is in every way as good as that made by the Dutch process.*

Other white substances, cheaper than hydroplumbic carbonate, have been suggested as substitutes for it, but none have been found which possess the peculiar properties of this substance. It "covers" remarkably well. It also appears to have some special and favorable chemical action upon the oil employed. An objection, however, may be urged against it on the ground that upon exposure to sulphuretted hydrogen — which exists frequently in the atmosphere — it is apt to blacken, from the formation of lead sulphide, PbS.

The pulverized mineral, heavy spar — barium sulphate, $BaSO_4$ — is often used to adulterate white lead. Zinc oxide, called zinc white, ZnO, is sometimes used as a substitute for white lead when there is a special reason to apprehend the injurious action of sulphuretted hydrogen.

Lead chromate, chrome yellow, $PbCrO_4$, is produced by adding an alkaline chromate, for example, potassium dichromate, $K_2Cr_2O_7$, to a soluble salt of lead. It appears as a beautiful yellow precipitate. Several different lead chromates are known, having formulas slightly varying from that already assigned. They vary in shade of color according to their composition. Strangely enough, however, some of the darker or more orange chromes contain relatively *less chromium* and more lead. The different varieties are largely used as pigments.

Lead acetate, sugar of lead, $Pb(OOC{\cdot}CH_3)_2$, is usually produced by the action of acetic acid upon lead oxide. It is a white salt, largely employed in the arts, especially in calico printing.

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* *Sci. Amer. Supp.*, Dec. 14, 1895, p. 16,643.

BOOK V.—FIFTH PERIODIC GROUP.

1ST SECTION.—VANADIUM, COLUMBIUM (NIOBIUM), NEODYMIUM, PRASEODYMIUM, SAMARIUM, TANTALUM.

2ND SECTION.—ARSENIC, ANTIMONY, ERBIUM, BISMUTH.

General Comments on the Group.

The metals of this group belong to the family containing nitrogen and phosphorus. They show a marked tendency to form, among other compounds, acid anhydrides, of the general formula M_2O_5, and thence metallic salts.

None of the metals of this group (not even arsenic, antimony, and bismuth) are very abundant in the earth. Columbium, neodymium, praseodymium, samarium, erbium (and terbium), are exceedingly rare; several of them being ordinarily found in minerals containing the rare yttrium earths. It is very doubtful even if erbium (and terbium) are really elementary substances.

Arsenic and antimony are often classified as non-metals. Certain of their properties make such classification convenient and appropriate. Thus, they combine with hydrogen to form the *gaseous* compounds, AsH_3 and SbH_3, respectively, as nitrogen and phosphorus form the gaseous compounds, NH_3 and PH_3, respectively.

Sir Henry E. Roscoe, eminent English chemist.

VANADIUM; V; 51, 38.

Data for Reference.

Density of solid vanadium, 5.5 (water being the standard = 1).

The metal does not melt except at very high temperature.

Vanadium was discovered by Del Rio in 1801, in a Mexican lead ore; he called the element erythronium. Neither the element nor the name was accepted, but in 1830, Sefström, discovering a new element in the smelted product of a Swedish iron-ore, called it vanadium. (Later it was proved to be the same as Del Rio's erythronium.)

The word vanadium is derived from *Vanadis*, the name of a Scandinavian goddess.

Vanadium has not been found uncombined in the earth. While it is very widely diffused in the earth, e. g., in iron ores and clays, its total amount appears to be very small.

Its principal source is the mineral vanadinite: a vanadate of lead, with lead chloride, $3Pb_3V_2O\cdot{}_5PbCl_2$. But a kind of coal, recently discovered in Argentina, has been found to yield ashes containing 38% of vanadium pentoxide, V_2O_5.

Metallic vanadium was produced by Henry E. Roscoe (now Sir Henry) in 1867, by heating vanadium chloride in a current of hydrogen gas.

So very large a number of compounds, some of them very complex, have been produced, that it is hardly practicable even to summarize them here. The following list, therefore, while it presents a few typical compounds, gives but an imperfect idea of the number and variety of those known.

A Few Compounds Containing Vanadium.

With chlorine;	Vanadium dichloride,	VCl_2		
	——— trichloride,	VCl_3		
	——— tetrachloride,	VCl_4		
With oxygen;	Vanadium monoxide,	V_2O		
	——— dioxide,	V_2O		
	——— trioxide,	V_2O_3		
	——— tetroxide,	V_2O_4		
	——— pentoxide,	V_2O_5;	Metavanadic acid,	HVO_3
			Sodium metavanadate,	$NaVO_3$
			——— orthovanadate,	Na_3VO_4
			——— pyrovanadate,	$Na_4V_2O_7$
			——— tetravanadate,	$Na_2V_4O_{11}$
			——— hexavanadate,	$Na_2V_6O_{16}$
			Ammonium metavanadate,	NH_4VO_3

With sulphur; Vanadium	disulphide,	V_2S_2
———	trisulphide,	V_2S_3
———	pentasulphide,	V_2S_5

Ammonium metavanadate, NH_4VO_3, is an important compound. It produces a very deep black liquid with tincture of gall nuts; Berzelius used this liquid as an ink.

Some demand for vanadium salts has arisen since it was observed that vanadium produces, with chloride of aniline or other aniline salts, a most intense form of aniline black.

COLUMBIUM; Cb (or Niobium; Nb) 93, 73.

Data for Reference.

Density of solid columbium, 7.06 (water being the standard = 1).

Fusing point of solid columbium, unknown.

Columbium, in a nearly pure form, was produced by Blomstrand in 1864-5, although the element was recognized as early as 1802.

The word columbium is derived from *Columbia*, North America.

The word niobium (generally used in Europe) is derived from Niobe, the name of a goddess of the Greek mythology.

Toward the close of the seventeenth century a specimen of the mineral now known as columbite (a columbate and tantalate of iron and manganese), was sent by Gov. John Winthrop of Connecticut, to Sir Hans Sloane, president of the Royal Society. About 100 years later this specimen came into the hands of the English chemist Hatchett, for examination. Hatchett, in 1801 or 1802, gave the name columbium to the rare metal he discovered in this mineral. Forty-five years later Rose, the German chemist, in studying the columbite of Brodamise, rediscovered columbium, but supposing his observation to be new, gave to the rare metal the name niobium. This latter name has obtained wide currency, but improperly so.

Columbium exists in several rare minerals, as samarskite and euxenite.

The element has been prepared from several of its compounds (difficult of preparation), by heating in an atmosphere of hydrogen.

A very large number of compounds, some of them very complex, have been produced: two chlorides, $CbCl_3$, $CbCl_5$; three oxides, CbO, CbO_2, Cb_2O_5; several acids, e. g., $HCbO_3$; and many salts of the columbium acids.

NEODYMIUM; Nd; 140, 8.—PRASEODYMIUM; Pr; 143, 6.

Data for Reference.

Density of the solid metals, about 6.54 (water being the standard = 1).

As early as 1842 Mosander recognized a new metal in the mineral cerite. As it seemed to have a very close relationship to lanthanum, found in cerite, it was named didymium, from the Greek word *δίδυμος*, (*didymos*) two-fold.

In 1885, Auer von Welsbach proved that the so-called didymium contains two elements. One of these, producing an oxide which is dark brown, and salts which are light green, he called praseodymium (*πρασσαῖος*, *prassaios*, leek-green), the other producing an oxide, which, when heated, is blue, and salts which are amethyst colored, he called neodymium (*νέος*, *neos*, new).

(The name didymium, still used in most works on chemistry, must now be discarded.)

These elements should be considered as related to the rare yttrium metals with which they are associated in natural minerals. (See pp. 176-179)

Compounds of these metals follow the types MCl_3, M_2O_3, M_2SO_4, MNO_3, etc.

SAMARIUM; Sm; 150, 26.

This very rare metal appears to have been recognized first by Delafontaine in 1878: he observed that when effort is made to prepare compounds of *didymium* (see above) from samarskite the product is contaminated by compounds of a substance not previously described. To the metal thus represented he gave the name *decipium*. In 1879, Lecoq de Boisbaudran, by careful spectroscopic examination of similar material, recognized certain new lines, which he referred to a new metal, which he called *samarium*.

There is still much doubt as to the distinct elementary character of the substance. Prepared from samarskite and orthite, it must be considered as in nature associated with the yttrium metals. (See pp. 176-179.)

Its compounds are believed to be after the types MCl_3, M_2O_3, M_2O_5, $M_2(SO_4)_3$, $M(NO_3)_3$.

TANTALUM; Ta; 182, 84.

In 1802, Ekeberg recognized a new metal in certain minerals; later it was shown that his product contained columbium, (niobium); still further investigation revealed the fact that both columbium and another new metal were present. To the latter metal the name tantalum (from Tantalus, Greek deity,) was given.

Tantalum occurs in certain minerals in association with columbium. Thus, tantalite found in Finland and Sweden contains oxides of tantalum and columbium, Ta_2O_5 and Cb_2O_5, respectively, together with oxides of tin, iron, and manganese; columbite found in Massachusetts and elsewhere, contains the oxides of tantalum and columbium just mentioned, together with oxides of tungsten, tin, zirconium, iron, manganese, and magnesium. Fergusonite contains the oxides of tantalum and columbium just mentioned, and, in addition, oxides of tungsten. tin, yttrium, erbium, cerium, uranium, and of other metals.

Apparently, pure tantalum has not been produced.

A large number of compounds of tantalum have been formed and studied. As examples may be given: a chloride, $TaCl_5$; an oxide, Ta_2O_5; many tantalates, as $NaTaO_3$, and others much more complex.

ARSENIC; As; 75,01.—ANTIMONY; Sb; 120,43.

These elements are mentioned here because they are often classified among the metals. But it seems preferable to discuss them among the non-metals. The reader is referred to the Author's work, *Chemistry of the Non-Metals.*

TERBIUM; Tb; 160.

The name of this element has long held a place in the list of metals. The substance is stated to exist in gadolinite and samarskite. But much doubt exists as to its elementary character. (See pp. 176-179.)

It is assumed to form compounds after the type M_2O_3.

ERBIUM; E; 166, 32.

The name erbium is applied to a metal supposed to exist in gadolinite and samarskite. But the metal itself has not been isolated satisfactorily, nor is it at all certain that so-called compounds of it represent pure substances. (See pp. 176-179.)

It is usual to assume that it forms compounds of the type E_2O_3.

BISMUTH; Bi; 208, 11.

Data for Reference.

Density of bismuth, 9.759 (water being the standard = 1).
Fusing point of solid bismuth, about 268.3° C.
Boiling point of liquid bismuth, between 1090° and 1450° C.
Bismuth was recognized by Basil Valentine in the 15th century.
The word bismuth is of obscure origin.

Bismuth is found in small quantities in the *native*, that is, in the free or uncombined form. It also occurs in a large number of ores. Thus, it is known in the form of an oxide called bismuth ochre, Bi_2O_3. It is found occasionally as a sulphide called bismuthite, Bi_2S_3. It exists in several minerals in association with other elements, as tellurium, copper, lead, vanadium, selenium.

Bismuth was formerly prepared mostly from native bismuth by a very simple smelting operation whereby the metal, which easily melts, was allowed to run away from the earthy impurities.

At present, owing to the relatively high price of bismuth and modern metallurgical knowledge, bismuth is obtained from ores which contain it in combination with other substances. In such cases the ore is usually roasted so as thoroughly to oxidize certain

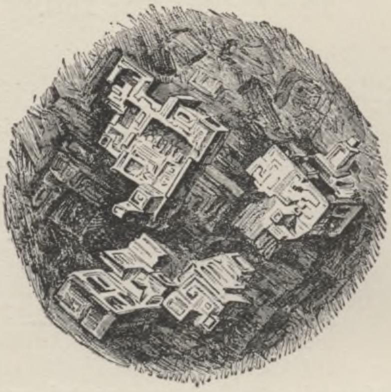


Fig. 74. Metallic bismuth upon hardening, after fusion, forms crystals.

constituents of the ore, and to volatilize others. The roasted product is subjected to fluxing processes or else to wet processes, according to the character of the ores employed.

Bismuth is sometimes obtained incidentally in the cupellation of silver lead produced from ores containing bismuth. After the silver has been removed, the bismuth, as an oxide, is found associated with the lead oxide produced during cupellation. From this lead oxide the bismuth oxide may be dissolved by use of hydrochloric acid. To the solution a large quantity of water is added. This throws down a white precipitate of bismuth oxychloride, $BiOCl$. Subsequently the basic salt is smelted with sodium carbonate and carbon, whereby the metallic bismuth is easily obtained.

Bismuth is hard and brittle. It has a beautiful metallic lustre, whitish, tinged with pink. It melts at a comparatively low temperature; and, when cooling, it forms crystals which appear to be cubical, but are not strictly so.

The bismuth of commerce is rarely pure. It may contain, according to its original mineral source, traces of iron, copper, lead, silver, antimony, tin, sulphur, and even minute quantities of arsenic. These impurities, and especially the latter one, are of great importance if the metal is to be employed for the manufacture of medicinal salts. In this case the metal must be subjected to further purification.

A Few Compounds of Bismuth.

With fluorine;	Bismuth fluoride,	BiF_3
With chlorine;	—— chloride,	$BiCl_3$
	—— dichloride,	Bi_2Cl_4
With bromine;	—— bromide.	$BiBr_3$
	—— dibromide,	(?)
With iodine;	—— iodide,	BiI_3

With oxygen;	Bismuth dioxide,	Bi_2O_2		
	——— trioxide,	Bi_2O_3		
	——— tetroxide,	Bi_2O_4		
	——— pentoxide,	Bi_2O_5;	Bismuthic acid,	$HBiO_3$
	——— oxychloride,	BiOCl		
With sulphur;	Bismuth sulphide,	Bi_2S_3;	Bismuth sulphate,	$Bi_2(SO_4)_3$
With selenium;	——— selenide,	Bi_2Se_3		
With nitrogen;			Bismuth trinitrate,	$Bi(NO_3)_3$
			Basic bismuth nitrate,	$Bi(OH)_2NO_3$
With phosphorus;			Bismuth phosphate,	$BiPO_4$
With carbon;			Bismuth carbonate,	$Bi_2O_3CO_2$

Bismuth trichloride, $BiCl_3$, is produced when powdered bismuth is heated in a current of chlorine gas. Bismuth trichloride is also formed when bismuth trioxide is warmed in strong hydrochloric acid. This chloride manifests a property decidedly characteristic of bismuth compounds, namely, it is easily decomposed when it is poured into cold water, bismuth oxychloride, BiOCl, being formed.

Bismuth trioxide, Bi_2O_3, may be produced by heating the carbonate or the nitrate of the metal. The volatile acid is expelled, and the oxide remains as a yellow powder.

Basic bismuth nitrate, $Bi(OH)_2NO_3$, is produced when a solution produced by dissolving metallic bismuth, or bismuth trioxide in concentrated nitric acid is thrown into a large quantity of cold water. The basic nitrate appears as a white precipitate.

This is one of the principal commercial compounds of bismuth. It is largely used as a medicine in certain disorders of the digestive tract.

It is also employed to some extent as a cosmetic or face powder. Sometimes, unfortunately, however, a cheap substitute is found in a hydrocarbonate of lead. This latter substance is somewhat poisonous to the skin.

Basic bismuth nitrate is somewhat employed to produce a glaze upon porcelain.

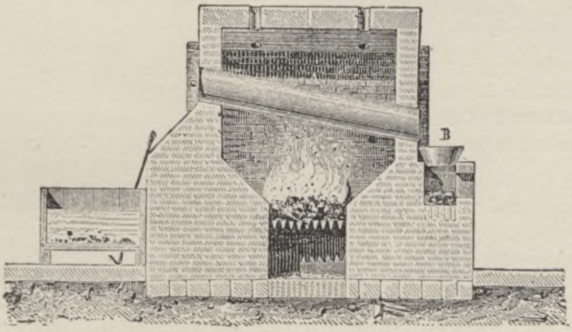


Fig. 75. Section of furnace for obtaining bismuth from *native* ore. The ore is gently heated in the inclined retort.

BOOK VI.—SIXTH PERIODIC GROUP.

CHROMIUM, MOLYBDENUM, TUNGSTEN, URANIUM.

The metals of this group have atomic weights very remote from one another; Cr, 52.14; Mo, 95.99; W, 184.83; U, 239.59.

In somewhat similar manner the specific gravities vary: Cr, 6.5; Mo. 8.5: W, 18—19; U, 18.5.

They are not fusible except at very high temperatures.

They form compounds after the types MO, M_2O_3, MO_2, MO_3, etc. The lowest oxide is not easily formed. The higher oxides are more common. The oxides of the type MO_3 are acidic, and they give rise to the formation of many metallic salts.

The metals of this group are capable of forming large numbers of compounds, *many of them of very complex constitution.*

CHROMIUM; Cr; 52, 14.

Data for Reference.

Density of solid chromium, 6.5—6.8 (water being the standard = 1).

Fusing point of solid chromium, above 2500° C.

Chromium was discovered by Vauquelin in 1797.

The word chromium is derived from the Greek word χρῶμα (*chroma*), color.

Distribution of Chromium.

Chromium is not found in the earth free or uncombined.

Its most important mineral is that called chrome iron ore or chromite, $FeCr_2O_4$.

This formula suggests a relationship to magnetic iron ore, Fe_3O_4. The difference between them is that in chromite two atoms of chromium take the place of two atoms of iron in the magnetite. A further resemblance is noted in that crystals of chromite are isomorphous with those of magnetite.

Another ore of chromium is that called crocoisite, lead chromate, $PbCrO_4$.

A considerable number of minerals contain relatively small quantities of chromium; to these it usually gives color—thus the emerald is said to owe its green hue to chromium.

Preparation and Properties of Chromium.

The metal chromium is not easily prepared. It may be obtained, however, by the action of some powerful reducing agent upon suitable compounds of chromium. Wöhler obtained chromium as follows:

He fused a mixture containing chromic chloride with sodium chloride and metallic zinc. In due time he obtained a sort of alloy (called a regulus), consisting of zinc and chromium. Upon dissolving the zinc with dilute nitric acid, the metallic chromium was left in the form of a powder.

Chromium has also been obtained by the influence of metallic sodium upon other compounds. It has also been obtained by heating carbon with certain chromic compounds.

Chromium is a very hard metal and it is very difficult of fusion.

A very large number of compounds of chromium have been produced; almost without exception they are colored, a great variety of hues being represented.

A Few Compounds Containing Chromium.

With fluorine	Chromic fluoride,	Cr_2F_6		
With chlorine;	Chromous chloride,	Cr_2Cl_4		
	Chromic ——	Cr_2Cl_6		
With bromine;	Chromous bromide,	$CrBr_2$		
	Chromic ——	Cr_2Br_6		
With iodine;	Chromium iodides,	?		
With oxygen;	Chromium monoxide,	CrO;	Chromous hydroxide,	CrO_2H_2
	Chromo-chromic oxide,	Cr_3O_4;		
	Chromium sesquioxide,	Cr_2O_3;	Chromic hydroxide,	$Cr_2O_6H_6$
	—— trioxide,	CrO_3;	Chromic acid,	H_2CrO_4
With sulphur;	Chromium monosulphide,	CrS;	Chromous sulphate,	$CrSO_4$
	Chromic sulphide,	Cr_2S_3;	Chromic sulphate,	$Cr_2(SO_4)_3$
	(other sulphides)			
With nitrogen;	Chromium nitride,	CrN;	Chromic nitrate,	$Cr(NO_3)_3$
With phosphorus;			—— phosphate,	$Cr_2(PO_4)_2$
With carbon;			Chromous carbonate,	$CrCO_3$
With metals;			Potassium chromate,	K_2CrO_4
			—— dichromate,	$K_2Cr_2O_7$
			(many other chromates)	
			Zinc chromite,	$ZnCr_2O_4$

Chromium, in association with ammonium or ammonium compounds, enters into a series of molecular groups to form compound radicles which in turn unite with elements and other radicles to form numerous series of complex salts. This volume is not appropriate for their discussion but the following list of several of the classes of them is suggestive:

1st class: Chromtetrammonium salts,
2d " Purpureochrom salts,
3d " Roseochrom salts,
4th " Xanthochrom salts,
5th " Luteochrom salts,
6th and 7th classes: Rhodochrom and Erythrochrom salts.

Potassium dichromate, $K_2Cr_2O_7$, the chief commercial salt of chromium, is prepared directly from chrome iron ore. The chrome iron ore is first oxidized by a roasting process. It is then heated with potassium carbonate and quicklime, under oxidizing conditions. Under these circumstances, either potassium chromate or potassium dichromate is produced. If the proportions are not properly adjusted, some calcium chromate may be formed. At all events, the mass is treated with the smallest practicable amount of water, and the mixture is filtered.

The solution is examined and its condition learned. If it contains potassium dichromate, this salt is secured by the operation of crystallization. If it contains calcium chromate, potassium sulphate is added for the purpose of replacing the calcium by potassium. If it contains the so-called neutral potassium chromate, sulphuric acid is added which withdraws a portion of the potassium, affording potassium dichromate, the substance desired.

Potassium dichromate forms orange red crystals, soluble in a small amount of water.

Potassium dichromate is largely used in the arts.

First, it is used as *the source of other chromium compounds*, especially of chrome yellow, chrome alum, and Guignet's green.

Second, it is largely employed in dyeing and calico printing.

In the dyeing of wool with logwood, potassium dichromate produces an excellent black, and it is largely used for this purpose, The chromium compound has a double action. On the one hand, it oxidizes the coloring material of the logwood, an action distinctly favorable to the production of black; on the other hand, the chromium acts as a mordant, combining with the oxidized coloring matter to produce a new black compound within the fibre of the cloth.

In calico printing, it is employed for purposes somewhat similar to the foregoing. It is also employed for the production of chrome yellow upon the cloth. In this case, of course, a salt of lead, usually acetate or nitrate, is used.

Third, It is used in certain photographic processes. Many of these depend on the relations of potassium dichromate to gelatine. If a mixture of these substances is placed upon glass or paper, the film is sensitive to light. The chemical rays of light have a two-fold action upon the chromatized gelatine. In the first place, the light determines a decomposition of the chromium compound, producing thereby certain dark colored oxides of chromium; in the second place, the potassium dichromate *renders insoluble in water that portion of gelatine which has been exposed to sunlight*, other portions being still soluble. When, therefore, an exposed plate is washed with water, *those parts where the sunlight has fallen remain insoluble*, and those parts where the sunlight has not fallen dissolve and wash away. So distinct is this action that an exposed film, after washing, forms a sort of engraving which may be used for printing with ink; or by pressure into soft metal, it may afford a sort of stereotype capable of subsequent use for printing with ink.

Chrome alum, $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$, may be prepared from potassium dichromate by addition, first, of sulphuric acid; then of ethyl alcohol or some other reducing substance; these operations being followed by crystallization. One portion of the sulphuric acid forms potassium sulphate and liberates chromic oxide. After the chromic oxide has been reduced by the alcohol, another portion of sulphuric acid combines with it to form chromic sulphate. Then the chromic sulphate unites with the potassium sulphate, producing chrome alum.

Chrome yellow, plumbic chromate, is produced as a precipitate when a solution of potassium dichromate is added to a solution of a soluble salt of lead. If the chrome yellow is treated with some alkaline material in limited amount, as sodium hydroxide or calcium hydroxide, a portion of the chromium is withdrawn, and chrome orange is produced.

The deepening color is remarkable, since it is associated with a lessening of the amount of chromium in the compound. (The anomaly consists in the fact, that, ordinarily speaking, the color of the compound is referable to chromium rather than to any other element present.)

Chrome yellow is employed not only in calico printing and in the coloring of other cotton goods, but also as a pigment in oil painting and in water color painting, and in the printing of wall papers and other papers.

Many other chromates are highly colored: silver chromate, mercury chromates, and others, being reddish or brownish in hue. Barium chromate, calcium chromate, zinc chromate, are all light-yellow compounds.

MOLYBDENUM; Mo; 95, 99.

Data for Reference.

Density of solid molybdenum, 8.6 (water being the standard = 1).

Fusing point of solid molybdenum, unknown (does not fuse at a white heat).

In 1778, Scheele produced a new compound from molybdenum glance, a mineral. In 1782, Hjelm prepared molybdenum from Scheele's compound.

The word molybdenum is derived from the Greek word, μολύβδαινα (molybdaina), used by Dioscorides and Pliny to designate galena and similar heavy minerals.

Molybdenum has not been found free, uncombined, in the earth.

It exists, in combination, in several minerals. The most important are molybdenite, molybdenum disulphide, MoS_2, and wulfenite, plumbic molybdate, $PbMoO_4$.

Molybdenite is found in many parts of Europe. It is found also in Connecticut, Texas, and California.

The metal molybdenum has been produced by heating certain of its compounds with carbon, or with sodium, or with hydrogen, or by electrolysis.

Molybdenum is a dull, silver-like metal.

Molybdenum compounds, in immense number, have been produced, especially a great variety of molybdates. Of many of the compounds the exact molecular constitution is yet unknown.

A Few Compounds Containing Molybdenum.

With chlorine;	Molybdenum dichloride,	$MoCl_2$	
	——— sesquichloride,	Mo_2Cl_6	
	——— tetrachloride,	$MoCl_4$	
	——— pentachloride,	$MoCl_5$	
With oxygen;	Molybdenum monoxide,	MoO	
	——— sesquioxide,	Mo_2O_3	
	——— dioxide,	MoO_2	
	——— trioxide,	MoO_3;	Molybdic acid, H_2MoO_4
			Potassium molybdate, K_2MoO_4
			Ammonium molybdate, $(NH_4)_2MoO_4$

Besides the typical compounds above mentioned, molybdenum forms a variety of others, too numerous and complex to admit of even a summary here.

Neither molybdenum nor its compounds have any considerable uses in the arts.

In chemical analysis, a nitric acid solution of ammonium molybdate is generally employed for the precipitation of phosphoric acid. Under proper conditions, it thus produces a fine, powdery yellow precipitate, called ammonium phospho-molybdate. It contains about three per cent. of phosphoric oxide, P_2O_5. It is said to have the formula $2(NH_4)_3PO_4 \cdot 22MoO_3 \cdot 12H_2O$. The yellow compound dissolves promptly in ammonium hydroxide.

TUNGSTEN; W; 184, 83.

Data for Reference.

Density of solid tungsten, in form of powder, 19.13 (water being the standard = 1).

Fusing point of solid tungsten, unknown.

In 1785, the brothers J. and F. d'Elhuyan produced the metal tungsten from a compound prepared from the mineral tungstein, by Scheele, in 1781.

The word tungsten is derived from the Germanic word *tungstein*, (heavy stone) the name of a mineral.

The symbol W is the initial of the word wolfram, the name of a mineral containing tungsten.

Tungsten has not been found free, uncombined, in the earth.

It occurs in several minerals. One of the most important is that known as scheelite, calcium tungstate, $CaWO_4$. The mineral known as wolfram, or wolframite, is a tungstate of iron and manganese, $MnFeWO_4$.

The element has been prepared by reduction of certain of its compounds under the influence of heat, in presence of hydrogen or of carbon.

The metal has a grayish lustre. It is not easily attacked by acids. Like the other members of this Group, it forms a great number of compounds, many of them tungstates, and many of them of very complex molecular constitution.

A Few Compounds Containing Tungsten.

With chlorine;	Tungsten dichloride,	WCl_2		
	——— tetrachloride,	WCl_4		
	——— pentachloride,	WCl_5		
	——— hexachloride,	WCl_6		
With oxygen;	Tungsten dioxide,	WO_2		
	——— trioxide,	WO_3;	Tungstic acid,	H_2WO_4
			Sodium tungstate,	Na_2WO_4

Beside the typical compounds above mentioned, tungsten forms a variety of others, too numerous and complex to admit of even a summary here.

Neither tungsten nor its salts have any considerable uses in the arts, although sodium tungstates have been employed, to some extent, in admixture with starch to spread upon light cotton and linen fabrics with a view to making them fire-proof.

URANIUM; U; 239, 59.

Data for Reference.

Density of solid uranium, 18.33 (water being the standard = 1).

Solid uranium fuses at a bright red heat.

In 1789, Klaproth recognized a new element in the mineral called pitchblende, but he did not produce the pure metal. In 1840, Péligot isolated the metal.

The word uranium was applied by Klaproth in reference to the name of the planet Uranus, discovered shortly before he recognized the existence of the metal.

Uranium has not been found free, uncombined, in the earth.

In combination, it exists in a few minerals, sparsely distributed.

Its most important mineral is that called pitchblende, a substance found in Germany and to some extent in Cornwall, England; it consists mostly of uranoso-uranic oxide, U_3O_8, or $UO_2 \cdot 2UO_3$

A deposit of uranium ore yielding from twelve per cent. to thirty per cent. of the metal is reported in Cornwall, England. Heretofore, only small pockets of this ore have been discovered. The extreme rarity of uranium ores has given the metal a very high price. The new deposit is in the form of a true lode — a fissure vein. If the early statements prove true, the discovery is of importance.

The metal uranium has been prepared by heating certain of its compounds with sodium.

Uranium is a hard metal, of a white color somewhat resembling that of nickel.

The atomic weight of uranium is higher than that of any other known element.

The known compounds of uranium are very numerous, but not as much so as those of chromium, molybdenum, and tungsten.

Most of the salts of uranium have delicate colors, from yellow to light-green.

A Few Compounds Containing Uranium.

With chlorine;	Uranium trichloride,	UCl_3		
	——— tetrachloride,	UCl_4		
	——— pentachloride,	UCl_5		
With oxygen;	Uranous oxide,	UO_2		
	Uranoso-uranic oxide,	U_3O_8		
	Uranic ———	UO_3;	Uranic acid,	H_2UO_4
			Sodium uranate,	Na_2UO_4
			Potassium ———	K_2UO_4

Beside the typical compounds above mentioned, uranium forms a variety of others too numerous and complex to admit of even a summary here.

Oxides of uranium find some application in coloring glass. The color imparted is a delicate greenish-yellow called canary yellow; but such glass is expensive.

Uranium compounds have also some uses in photography, as a substitute for chloride of gold.

It is believed that if, in the future, a larger supply of uranium ores is discovered, the metal may be used in producing — with platinum and copper — gold-like alloys suitable for jewelry and electrical apparatus.

BOOK VII. — SEVENTH PERIODIC GROUP.

MANGANESE.

The metal manganese stands here as the single metal of a group, the position it receives in Mendeléeff's table. On certain accounts it may be with propriety associated with the iron series of the eighth group. Its atomic weight, its specific gravity, and many of its chemical properties ally it closely with iron, nickel, and cobalt.

MANGANESE; Mn; 54,99.

Data for Reference.

Density of solid manganese, 6.85 — 8.01 (water being the standard = 1).

Fusing point of solid manganese, about 1800° — 1900° C.

In 1774, Scheele recognized black oxide of manganese as containing a special metal; later the metal was isolated, first by Gahn.

The word manganese is the English form of a manufactured word of Latin form, ***manganesium***; it was constructed by slightly modifying the word magnesium. (See p. 162.)

Distribution of Manganese.

Manganese has not been found free, uncombined in the earth. It exists in several minerals which contain it in large proportion:

Pyrolusite,	MnO_2,
Braunite,	Mn_2O_3,
Hausmannite,	$Mn_2O_3 \cdot H_2O$,
Manganese blende,	MnS,
Manganese spar,	$MnCO_3$.

These minerals, especially the first mentioned, occur in considerably abundant deposits and widely distributed.

In smaller proportions manganese compounds are very widely distributed; they occur in ores (especially of iron) in sea water, in many amimal and vegetable substances. (Manganese is believed to exist in the sun's atmosphere also.)

Preparation and Properties of Manganese.

Metallic manganese may be prepared by decomposing certain oxides of the metal under the influence of carbon at high temperatures. The carbon withdraws oxygen ; the metal is left, though in an impure form. This kind of operation is usually conducted on a small scale, since metallic manganese is little used.

Metallic manganese is a white-grey lustrous metal, somewhat resembling iron. It is hard, brittle, capable of high polish, non-magnetic.

Manganese has been made to form a great many compounds, most of them colored ; the shades of color are very various, from flesh-colored to amethystine and red, and from green to black.

A Few Compounds Containing Manganese.

With fluorine ;	Manganous fluoride, MnF_2	
	Manganic ——— Mn_2F_6	
With chlorine ;	Manganous chloride, $MnCl_2$	
	other chlorides	
With oxygen ;	Manganous oxide, MnO ;	Manganous hydroxide, MnO_2H_2
	Manganoso-manganic oxide, Mn_3O_4 ;	
	Manganic ——— Mn_2O_3	
	Manganese dioxide, MnO_2 ;	Potassium manganite, K_2MnO_3
	Manganic anhydride (?), MnO_3 ;	Manganic acid, H_2MnO_4
		Potassium manganate, K_2MnO_4
	Permanganic ——— (?), Mn_2O_7 ;	Permanganic acid, $H_2Mn_2O_8$
		Potassium permanganate, $K_2Mn_2O_8$
With sulphur ;	Manganous sulphide, MnS ;	Manganous sulphite, $MnSO_3$
	Manganese disulphide, MnS_2 ;	Manganous sulphate, $MnSO_4$
		Manganic sulphate, $Mn_2(SO_4)_3$
With nitrogen ;		Manganous nitrate, $Mn(NO_3)_2$
With phosphorus;		Manganic phosphate, $MnPO_4$
With carbon ;	several carbides, MnC ; MnC_2 Mn_3C	Manganous carbonate, $MnCO_3$

Beside the typical compounds above mentioned, manganese forms a variety of others, too numerous and complex to admit of mention here.

Manganese dioxide, MnO_2, as the powdered form of the black mineral pyrolusite, is very largely employed in the preparation of chlorine for the manufacture of bleaching-powder. (See p. 153.)

Moreover it is the natural source from which most of the artificial compounds of manganese are prepared.

Manganese dioxide has long been used in the manufacture of glass. (See p. 62.)

An artificial compound of manganese, iron and carbon, called *spiegel-eisen*, or spiegel, is used in the manufacture of Bessemer steel (which see).

BOOK VIII.—EIGHTH PERIODIC GROUP.

1st Section.—IRON, NICKEL, COBALT.
2d Section.—RUTHENIUM, RHODIUM, PALLADIUM.
3d Section.—OSMIUM, IRIDIUM, PLATINUM.

The metals of the first section (to which manganese is sometimes added) are often spoken of as *the iron group.*

They are closely related in properties. The table below shows how nearly alike they are in atomic weights and specific gravities:

	(Mn)	Fe	Ni	Co
Atomic weight, ...	(54.99)	56.02	58.69	58.93
Approximate specific gravity....	(8.)	8.	9.	9.

Moreover they have high melting points, and they form chemical compounds of similar types.

The metals of the second and third sections are often called *the platinum metals*, and they are often classed (with gold) as *noble metals.* In nature they are all associated in platinum ores; in the metallic form they are resembling, white metals; they all show, though in different degrees, an aptitude toward the formation of complex ammonium compounds (as does also cobalt of the first section). They all have high atomic weights, high specific gravities, and high melting points (but the tables below show that they belong to sub-groups):

	Ru	Rh	Pd
Atomic weight, ...	101.68	103.01	106.36
Approximate specific gravity ...	12.3	12.1	11 4

	Os	Ir	Pt	(Au)
Atomic weight..............	190.99	193.12	194.89	(197.23)
Approximate specific gravity.	22.5	22.4	21.5	(19.3)

IRON; Fe; 56,02.

Introduction.— Distribution, preparation (metallurgical extraction, including production of steel), properties, uses, and compounds of iron.

Data for Reference.

Density of solid iron, 7.84 (water being the standard = 1).
Fusing point of solid iron, 1050° — 2204° C., according to quality.
Iron was known to the ancients (and apparently in very early times).
The derivation of the word iron is uncertain.

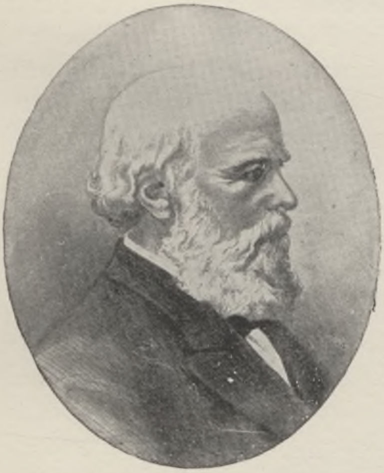
Introduction.

Iron is one of the most important and useful of metals.

Its ores are relatively abundant and widely distributed; moreover, they are often found in proximity to ample coal deposits — a circumstance very advantageous in connection with the smelting processes necessary.

Iron possesses certain remarkable properties. These fit it for extensive and varied uses in the three forms of cast iron, wrought iron and steel.

The iron industry has experienced a steady growth in recent years. New avenues of consumption have stimulated the manufacture and lowered the price of the product; again, fall in price has resulted in yet larger demand for the various forms of the metal. It is worthy of note that the production of iron in the United States has of late surpassed that of Great Britain — previously far ahead of every other country in this line. Apparently the United States is likely to retain its preëminence in this branch.



Sir Isaac Lowthian Bell, Bart., eminent English iron-master.

Fig. 77. Appearance of a meteorite which, with many others, fell in August, 1887, near the little town of Oshansk (Oshansk Government) Russia.

Distribution of Iron.

1—Iron does not occur to any considerable extent in an *uncombined* form in the earth. But meteoric stones which have been seen to fall to the earth from the sky have been found to contain considerable quantities of metallic iron in uncombined condition. True, they also contain certain other substances of which nickel may be said to be the most characteristic. In addition, cobalt, copper, manganese, carbon, sulphur, phosphorus, chlorine, and silicon, have also been found in meteorites.

But meteoric stones not containing metallic iron have often been seen to fall from the skies and bury themselves in the ground.

2—The chief ores of iron, like the ores of most of the heavy metals, consist of the element in question combined with oxygen or with sulphur. Iron is so widely diffused, sometimes in large mineral deposits, sometimes as what may be called mere impurity in minerals, that it may be accepted as a general statement that iron is found in the earth in more or less intimate combination with nearly all other substances.

3 — The most important ores of iron are represented in the following list:

Red hematite, or specular iron,	Fe_2O_3.
Magnetic iron (magnetite)	Fe_3O_4.
Brown hematite, (**limonite**)	$2Fe_2O_3 \cdot 3H_2O$.
Spathic iron,	$FeCO_3$.

Iron pyrites, FeS_2, is found in considerable abundance in the earth, as are also other sulphur compounds containing iron; but it does not ordinarily pay to work these ores *for the metal.* The sulphur is difficult to remove, and even a very small amount of sulphur is very injurious to the finished product. (But iron pyrites is often oxidized to ferrous sulphate, $FeSO_4$, called copperas, a salt considerably used in certain industries.)

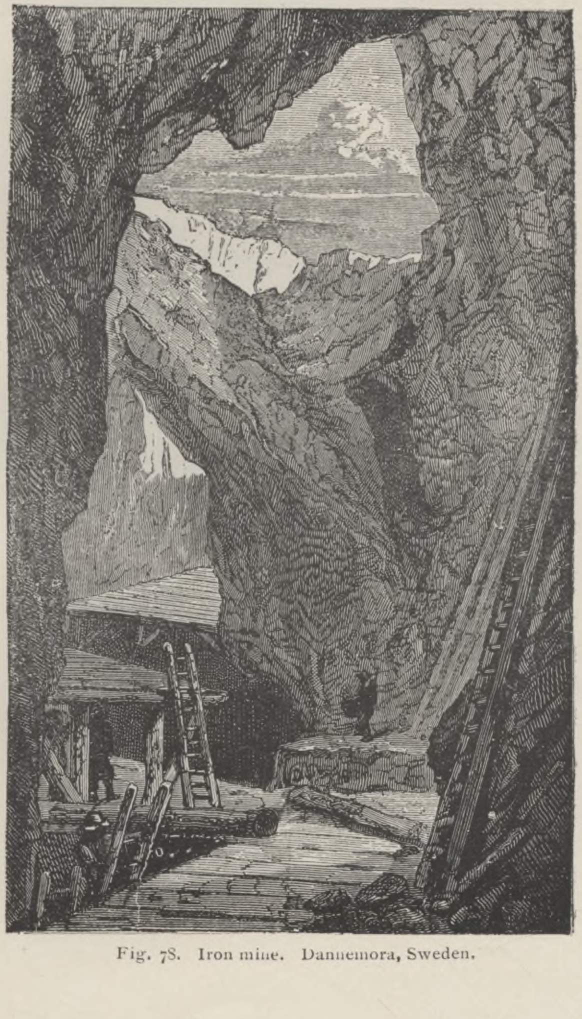


Fig. 78. Iron mine. Dannemora, Sweden.

Preparation of Iron.

In the laboratory, iron may be prepared from its compounds by several of those methods, described already (p. 8) as general processes for preparing metals — and referred to again and again by special examples in cases of preparation of metals already discussed :

1 — By heating an oxide of iron, e. g., ferric oxide, Fe_2O_3, *with carbon,* in a crucible in a furnace of considerable heating power. (But, as in case of many metals, the tendency is to produce a carbide — in this case cast iron — rather than the pure metal.)

2 — By heating an oxide of iron, e. g., ferric oxide, Fe_2O_3, in a glass tube in a *current of hydrogen gas.* The product is often called "iron by hydrogen."

3 — By *electrolyzing* an aqueous solution containing ferrous sulphate and ammonium chloride.

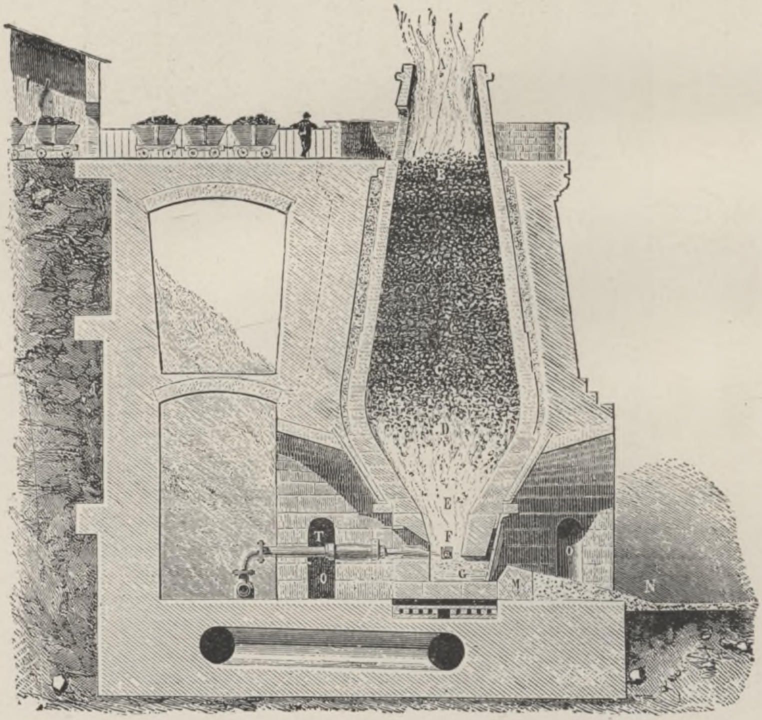


Fig. 79. Section of blast furnace in operation (using cold blast). The inner fire-brick lining is made separate from the outer structure, to allow for expansion.

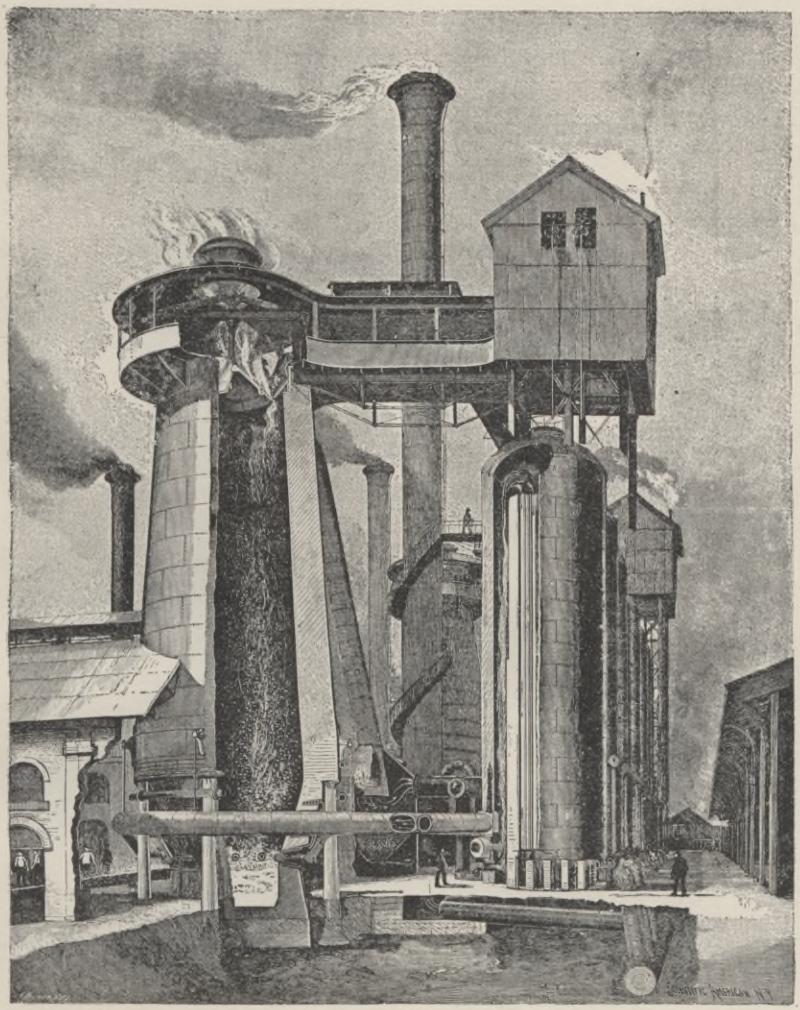


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Fig. 80. View (partly sectional) of most improved type of blast furnace plant, as used in the United States. There are two furnaces; two elevators, for the "charges"; three stoves for each furnace. From the left-hand furnace the "down-comer" (gas flue) enters a "dust-catcher" near the ground; thence, it leads to the stove. From the base of the stove, the "hot blast main" encircles the lower part of the furnace. The crucible of the furnace, containing molten iron, is shown, partly in section. At the left, is the casting house, where the pigs are cast. At the top of the furnace, the "cone and cup" arrangement is shown.

Metallurgical Extraction of Iron.

The so-called manufacture of iron may involve the production of the metal in three different important forms—*cast iron, steel, wrought iron.* But all three are compounds of iron with carbon, rather than the pure metal.

Cast iron is a compound of iron with about 4.5 per cent. of carbon; *Wrought iron,* on the other hand, contains less than .15 per cent of carbon; *Steel* is intermediate: it contains from .15 to 1.8 per cent. of carbon (but metal which is worked in a *fused* condition, as distinguished from a *pasty* condition, is called *mild steel,* even when it carries less than .15 per cent. of carbon).

Cast Iron.

In the metallurgy of iron the starting point is the production of cast iron. This substance may be employed as such for a variety of industrial uses; it may be turned into steel by removing a portion of its carbon; it may also be turned into steel by first removing the carbon so perfectly as to produce wrought iron and then,

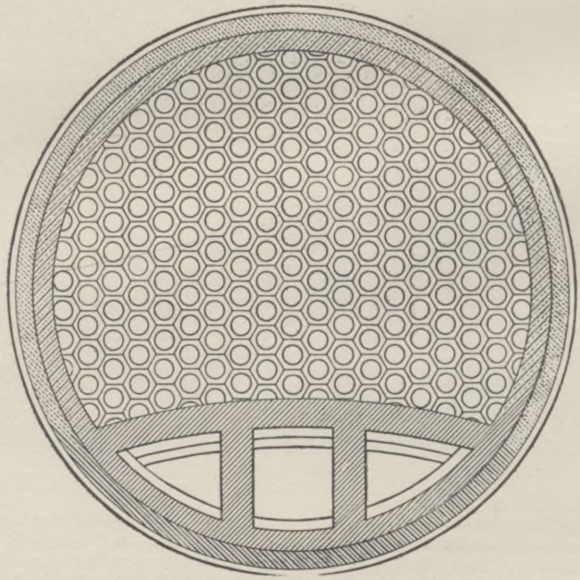

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Fig. 81. Section of Cowper stove. In the larger compartments, at one side, the furnace gases are burned with moderate air supply. The hot products of combustion pass downward through the smaller openings, and in so doing, heat the checker work. When the stove has been sufficiently heated, the cold air blast comes through it in a direction opposite to that just stated. (See section in fig. 80.)

adding a suitable amount of carbon to the wrought iron. These general principles furnish a guide as to the nature of the operations performed upon iron ores and upon metal derived from them.

The Blast Furnace.

This is, virtually, a large chimney, approaching one hundred feet in height. In its interior it is narrowest at the bottom, widest about one-third of the way from the bottom to the top.

— At the top it has a tight-fitting, cone-shaped cover, which may be lowered a little below a ring-shaped "cup," into the free space above the "burden" of the furnace.

— Just below the cover a large pipe is connected; its purpose is to convey unburned gases, from the top of the furnace downward, to the "stoves" where the gases are to be burned.

— At the base of the furnace is a tank-like receptacle — the "crucible"— for receiving the melted materials produced by the furnace: cast iron which sinks, and slag which floats.

— Entering the furnace, a few feet above its base, are a series of large blowpipes called "tuyeres." They deliver hot-air, under great pressure, to the fuel in the furnace. The air is pumped by blowing-engines, and it is heated by passing through the hot stoves. The tuyeres are kept cool by water jackets.

— The Cowper stoves, at least two (generally three) to each furnace, are chimney-like cylindrical structures containing brick checker-work. Stove A receives gas from the furnace; the gas, in burning, heats the checker-work; now the gas is sent to stove B, to heat it, in similar fashion. Air from the blowing engines is sent through the hot stove A; the stove heats the air, itself becoming cold. At the proper time the stoves are reversed. Thus stove A and stove B, alternately, receive furnace-gas to heat the stove — and air, to be heated by the stove.

— Near the top of the furnace is a charging house, in which the "charge" of material for the furnace, is delivered preparatory to its transfer to the furnace itself.

Operation of the Furnace.

— The working of the blast-furnace, in general, is as follows:

— Light fuel is thrown in and set on fire to warm the entire structure.

— The charge is introduced at the top, from time to time, and in layers. It consists of ore, fuel (coke), and flux (limestone).

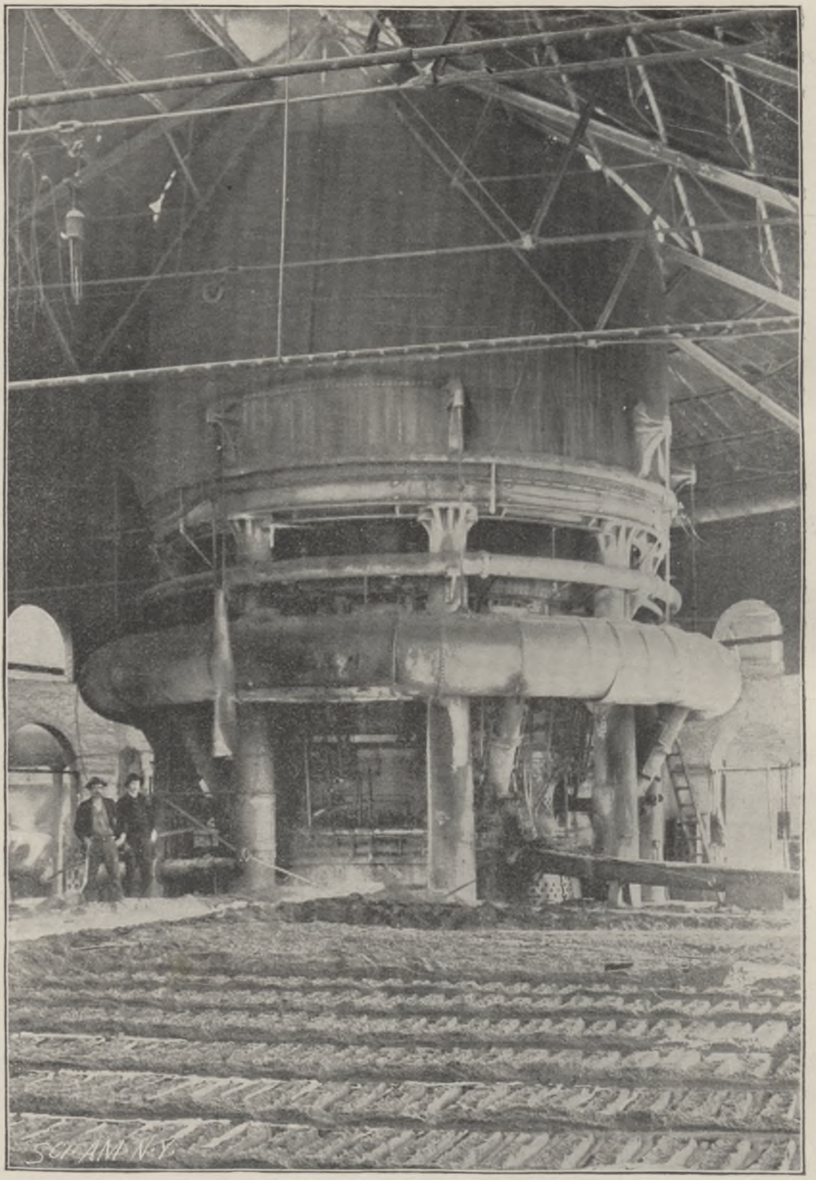

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Fig. 82. Base of the most improved form of hot blast iron furnace, as constructed in the United States. The structure is supported on heavy columns, carried by foundations deep in the ground. (See fig. 80.) The large pipe encircling the base of the furnace, and having downward branches, is the "hot blast main." Low down at the right is the "cinder trough," for taking away melted slag. Near the lower centre of the picture is the opening called the "iron notch," for drawing off melted cast iron to form pigs. The molds for the pigs are seen in the lower foreground.

Usually a load of ore is dumped upon the cone; the latter is lowered a little, and then the charge falls into the furnace. The cone is immediately raised, thus closing the upper opening. Later a mixture of coke and limestone is introduced, in a manner similar to that just described for the ore.

—The blast of air is started through the tuyeres. This stimulates the combustion of the fuel so that the lower portions of the burden become white-hot, undergo a variety of chemical changes, and become liquid.

—The melted materials fall in drops to the great crucible beneath the furnace. Here they separate into two layers — at the bottom, molten cast iron, above it, melted slag.

—The furnace may be kept "in blast" night and day for several years; the duration of continuous work depending upon the market demands for iron, as well as upon the skill with which the furnace is preserved from serious deterioration, and need of repairs.

Progress of the Charge.

It may be well now to trace the progress of the ore from the top of the furnace as it descends to hotter and hotter portions.

First. The ore, under the moderate heat near the top of the furnace, undergoes a very simple set of decompositions. Carbonated ores lose carbon dioxide; hydrated ores lose water. Next, the residual compounds meet with intensely hot carbon monoxide, CO, which speedily deprives them of oxygen, metallic iron being formed. The iron is at this time spongy and not very fusible.

Second. A little farther down, the lime, CaO, of the flux combines with silica, SiO_2, of the ore. A kind of glass, a fusible slag, silicate of lime, is formed.

Third. As the charge descends still farther it becomes hotter. The iron then enters into combination with carbon of the fuel, forming true cast iron; the slags, too, become more liquid. In addition more violent chemical changes, such as the union of iron with phosphorus and even with silicon, take place.

Fourth. The melted mass falls in liquid drops into the reservoir at the base of the furnace. Here separation takes place between the metal and the slag; the metal being heavier goes to the bottom; the slag being lighter comes to the top.

Fifth. The melted slag is drawn off by a spout at one side.

Sixth. The molten iron, as cast iron, is drawn off, from a relatively lower opening, and is cast into "pigs."

In case of most furnaces the pigs are formed in rough channels made in a bed of sand. In newer furnaces, the method is better: the melted iron is drawn into a large ladle; under this ladle moves a belt-like series of iron molds, each capable of forming a pig. As a given mold comes under the ladle, it is filled with melted iron, then the belt moves forward a step; thus, step by step, the molds are filled in succession. By the time a pig gets cool, its mold turns toward its return trip, then it empties its pig upon a truck. Before this mold is ready to receive another charge of melted cast iron, it is sprayed with milk of lime. It is thus at once cooled, and coated with a deposit of lime. (This latter material prevents the newly cast pig from adhering to the mold.) This system makes cleaner and more uniform pigs, and it dispenses with a good deal of hot and arduous hand labor.

Comments on the Working of the Blast Furnace.

The ore. In the case of most iron ores, except certain varieties of red hematite and magnetite, calcination, as a separate process, may precede smelting. The operation serves to remove carbon dioxide, water, and other volatile matters. It also partly removes sulphur that may be present in the form of pyrites. It oxidizes ferrous compounds; this is advantageous inasmuch as ferric oxide is less liable to be carried off in the slag. Finally, the ore is opened by the process, so that in the blast furnace the reducing gases act more readily on the iron compounds.

The fuel. One feature of advantage in the use of coke for the blast furnace, is the fact that in producing the coke, a considerable proportion of the sulphur of the coal has been expelled. Again, coke yields relatively less ashes than anthracite. Coke has this additional advantage over anthracite; coke is more porous. Thus, it allows the gases in the furnace to penetrate the mass more fully.

The following table gives the composition of the gases escaping from a British blast furnace:

Nitrogen,	N	55·35
Carbon monoxide,	CO	25·97
Carbon dioxide,	CO_2	7·77
Marsh gas,	CH_4	3·75
Ethylene,	C_2H_4	·43
Hydrogen,	H	6.73
		100.00

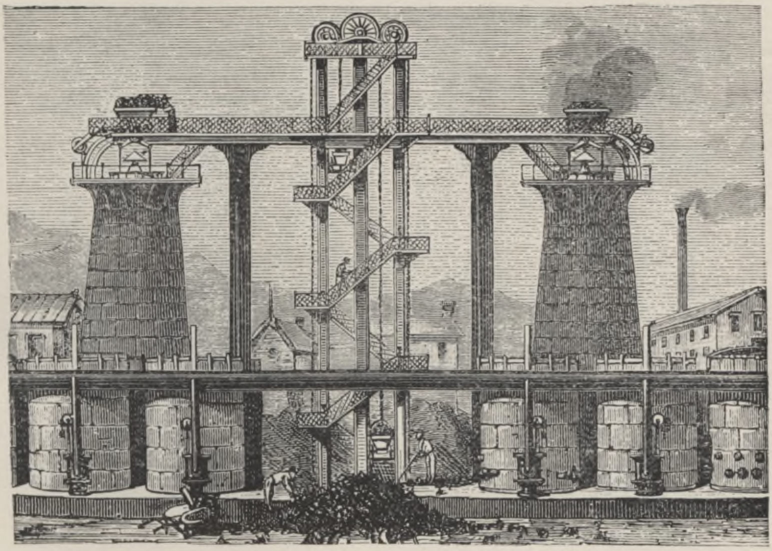

Fig. 83. French hot blast furnace for making pig iron. The low cylindrical structures in the foreground are the "stoves."

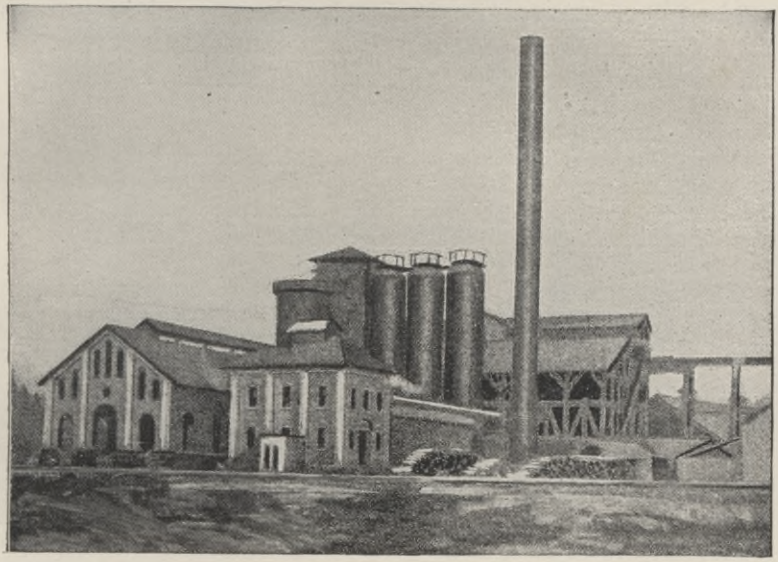

Fig. 84. Typical blast furnace plant of the southern part of the United States. The ore, the fuel, and the fluxes are brought in by the trestle, at the right. The tall chimney is made of wrought iron; the three cylindrical structures are the stoves; the cylindrical structure at the left is the blast furnace; the building at the extreme left is the pig-casting house.

A consideration of the table on p. 240 shows that the nitrogen escapes practically unchanged. (But a portion has formed ammonia gas, NH_3, or combined with elements otherwise.) The oxygen of the air has all entered into combination. The presence of carbon monoxide is discussed later; but it should be noted that it is a combustible gas, as are also marsh gas, ethylene, and hydrogen (the latter derived from the decomposition of water vapor from the air of the blast).

The action of carbon monoxide. Careful experiments have lately revealed the surprising fact that perfectly pure carbon cannot be burned in *perfectly dry* and pure oxygen. Moisture appears to be necessary.

Carbon monoxide is now recognized as the chief agent in reducing the oxides of iron. It does so in accordance with the equation

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

However, it has been recognized that the blast furnace usually gives off carbon monoxide. Since this is a combustible substance, it represents a loss of fuel.

The true solution of the problem has been found in gathering the furnace gases and burning them in the Cowper stoves. The heat generated is employed to heat the blast air, as already described.

Berthelot has recently shown a new way in which carbon monoxide may operate in the furnace, for he has found that the perfectly pure gas, when heated to a temperature of from 500 to 550° C., undergoes a kind of polymerization such that it partly separates into carbon and carbon dioxide.*

The hot blast. "In 1828, James Neilson recommended the use of the hot blast in direct opposition to the views of the most eminent metallurgists of the day. Four years after its introduction, at the Clyde works, their weekly output was doubled without the consumption of extra fuel (the air being heated to 300° C.)." The collection and utilization of the waste gases of the blast furnace has been so successfully carried out that it is said to have

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* Mond, Langer, and Quincke, have shown the remarkable fact that dry carbon monoxide at a temperature of 100° C., can take up metallic nickel to form a *gas* called nickel carbon oxide, $Ni(CO)_4$; and that from this, the nickel may be deposited at a temperature of 150° C. It has since been shown that iron forms a similar gaseous compound with carbon monoxide. Perhaps this compound is formed in the blast furnace; at any rate, it doubtless plays a part in some of the metallurgical operations in which iron and carbon are heated together.

Fig. 85. English blast furnace for production of pig iron.

accomplished a saving to English iron-masters of a million and a half tons of coal per annum.

The use of the hot blast is advantageous since it reduces the consumption of coal. It also enables the iron-master *to control the furnace better*; for if fusion or reduction does not proceed readily, that is if the burden is too pasty, a slight rise of the temperature of the blast may very promptly improve the action of the furnace. Again, if the burden melts too freely, a supply of cold air may thicken it to a proper consistency.

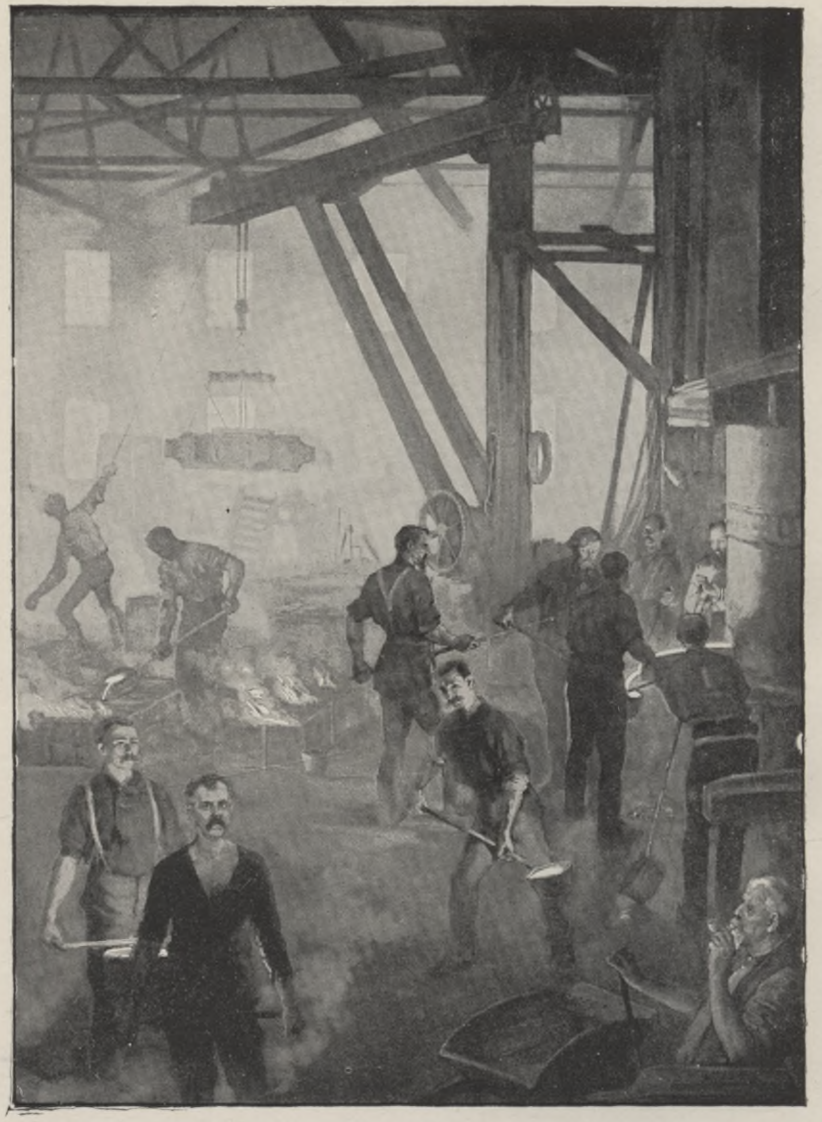


Fig. 86. View of interior of foundry. Pig iron is remelted in a high furnace called a cupola furnace, (partly shown at the right). The melted iron is run out into ladles of various sizes, according to need. From the ladles, it is poured into the sand molds to form castings.

Varieties of cast iron. The pig iron of commerce is divided into many sorts, all belonging to three grand divisions: *white cast iron,* which contains the carbon in the combined state; *gray cast iron,* in which part of the carbon is uncombined, but exists in minute black scales of graphite distributed through the mass; *mottled cast iron,* which is intermediate, containing carbon free and carbon combined. To these should be added a special variety called by its German name, *spiegeleisen* or simply *spiegel,* which is a white iron containing a large proportion of carbon, even as great as six per cent. (and often from five to twenty per cent. of manganese). Spiegel is largely used in the Bessemer process.

Uses of cast iron. The melting point of steel is intermediate between those of cast iron and wrought iron. Cast iron has the lowest melting point of the three. It is melted conveniently in a vertical furnace called a cupola furnace. In this furnace coke and pig iron are charged. In due time the iron melts; it sinks to the bottom of the furnace; thence is drawn out into ladles and poured into sand molds made to receive it. In such molds a variety of cast iron objects are formed. The establishment in which such work is conducted is called a foundry.

Wrought Iron.

Wrought iron may be manufactured from cast iron by the process called *puddling.* This process is conducted in a horizontal furnace called a reverberatory. Here the cast iron is melted; it is mixed with certain oxides of iron; it is stirred and worked by the laborer, called the puddler. Finally, it is withdrawn in large lumps called "blooms," and subjected to mechanical squeezing.

This change, from cast iron to wrought iron, is one in which certain constituents of the cast iron are *oxidized* and removed. But the wrought iron is less fusible than the cast iron from which it is derived. Therefore, the wrought iron produced is *pasty,* not *fused.*

In the puddling operation, the *melting* prepares the cast iron for subsequent operations. The *oxidizing* materials oxidize some of the carbon, silicon, phosphorus, and sulphur of the original metal. The *puddling* gathers the pasty wrought iron (when formed) into the "blooms." The *mechanical squeezing* expels impurities, including the slag formed during the puddling.

The old method of puddling is replaced to some extent by mechanical appliances. These are not only cheaper — they have the added advantage of relieving a certain number of men from hot and arduous labor. Mechanical puddling is conducted in large, cylindrical furnaces rotated by machinery.

Wrought iron differs from cast iron and steel in its chemical composition; that is, the wrought iron contains less than .15 per cent. of carbon, and it is worked in a pasty condition. Wrought iron is more fibrous and *less brittle* than cast iron. It is less fusible. It is *more malleable* and more *easily welded*. Its toughness fits it for many purposes for which cast iron is too brittle.

Wrought iron is not cast in molds as wrought iron is; it is *hammered or rolled* into shape by the process called, in general, *forging*.

Very minute amounts of certain substances when present in wrought iron, tend to alter the properties of the metal.

The influence of silicon upon iron is somewhat similar to that of carbon; it tends to harden it. Sulphur and phosphorus exert important and injurious action upon iron. Sulphur makes the

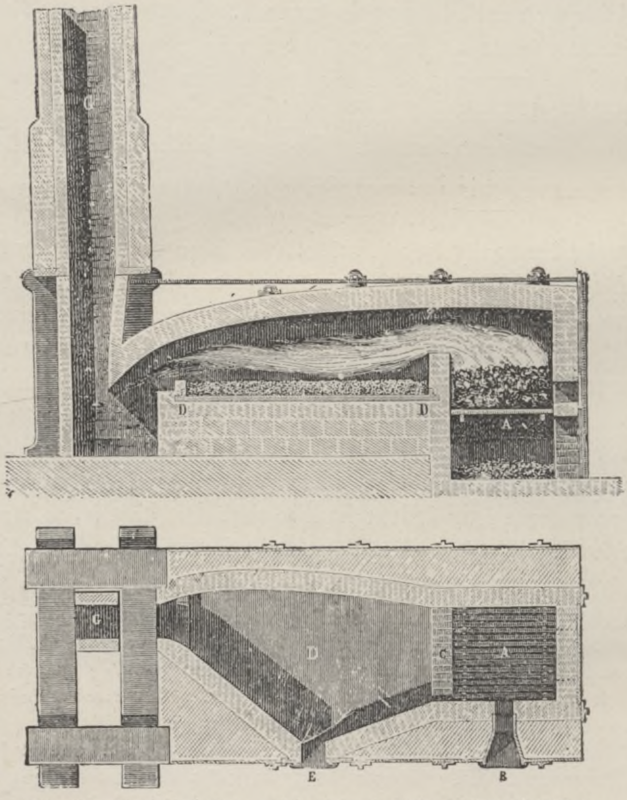


Fig. 87. Vertical section, and horizontal section, of reverberatory puddling furnace.

iron "red-short;" the hot metal loses the toughness of wrought iron and becomes brittle. Phosphorus, on the other hand, injures the iron when in the cold condition, making it "cold-short."

Steel.

It has already been noted that steel may be produced by *removing carbon from cast iron* or by *adding it to wrought iron.*

When wrought iron is packed in charcoal in an iron box, and in this condition is heated in a furnace, the carbon gradually makes its way into the iron, turning the latter into steel. Again, if wrought iron is melted and a highly carburetted cast iron, such as *spiegel,* is added to it, steel is produced.

The Bessemer Process.

The invention made by Henry Bessemer whereby Bessemer steel is produced is considered one of the most important ever made by man. The essential principle consists in blowing a current of air through melted iron, the original intention being to burn out carbon, and, if possible, other impurities. Mr. Bessemer's first published communication respecting his invention was in

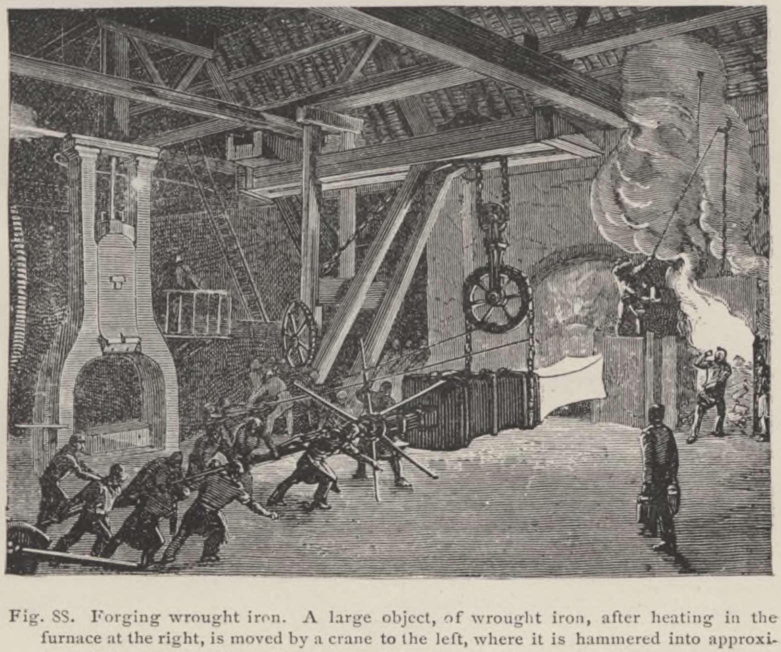


Fig. 88. Forging wrought iron. A large object, of wrought iron, after heating in the furnace at the right, is moved by a crane to the left, where it is hammered into approximately the required shape by the steam hammer.

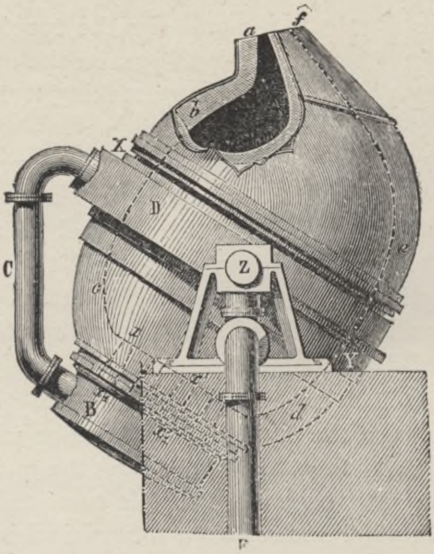


Fig. 89. Bessemer "converter," partly in section. The blast air enters at F, passes through the trunnion Z, round the converter by the air passage D, then through the tube C and the base B into the body of the converter. (See other pictures illustrating the Bessemer process.)

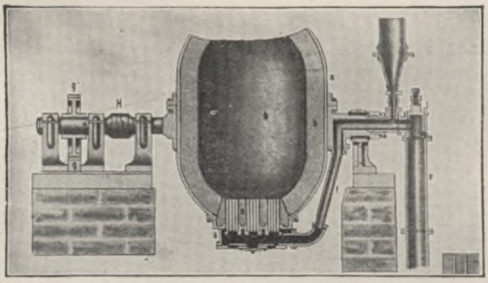


Fig. 90. Section of part of Bessemer converter and accessories.

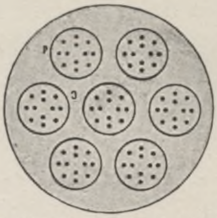


Fig. 91. Section through tuyeres of Bessemer converter.

1856. In this, he laid particular stress on the fact that the carbon, burned as described, furnished heat enough to carry on the process without the aid of additional fuel. Bessemer's invention as at present carried out may be described in brief as follows:

It employs *first*, a furnace in which to melt cast iron; *second*, another furnace in which to melt spiegeleisen; *third*, a special contrivance called a "converter." This is a vessel approximately egg-shaped, suspended on trunnions, on which it may be easily moved by means of hydraulic machinery. The top of the converter is open, though it varies in shape. The bottom of the converter is perforated, forming tuyeres, for the entrance of air. The interior of the converter is lined with some suitable powdered mineral material firmly rammed in place. Through the hollow trunnions, suitable air pipes are connected with the bottom of the converter.

Near the converter is a large pit circular in plan; in this pit, and around its margin, ingot-molds of iron, stand ready to receive the molten steel and to harden its exterior, so that an ingot may be handled by appropriate machinery, long before it is cool in its interior.

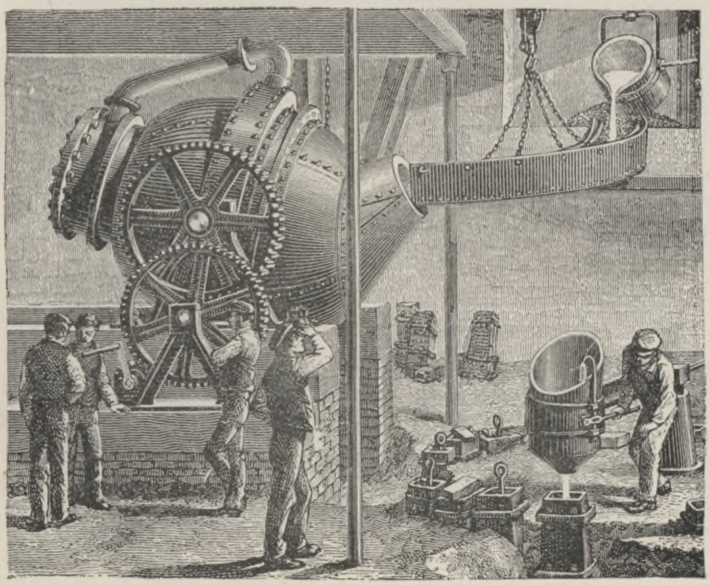
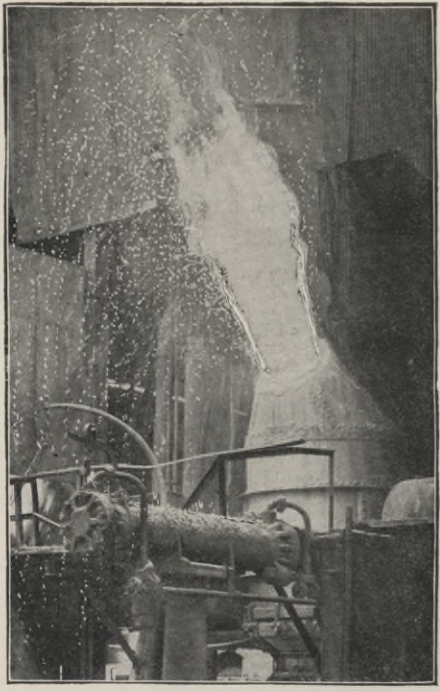


Fig. 92. Sketch of small, old style, Bessemer plant. High up at the right, a ladle is emptying melted *spiegel* into the converter. From its proper ladle, finished molten steel is flowing into an ingot mold.



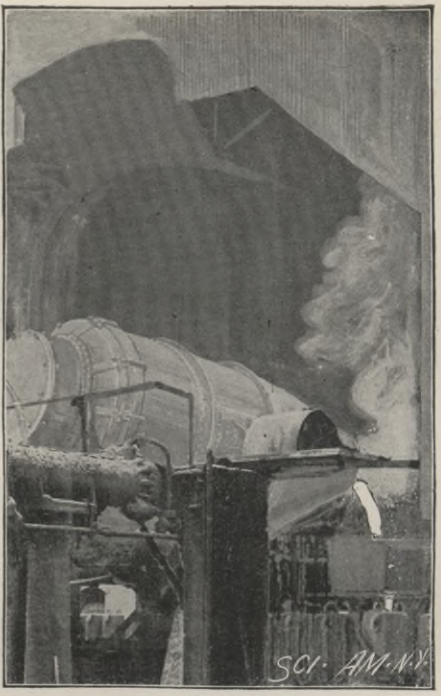


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Fig. 93. View of Bessemer converter during the blow; the cylindrical object in the lower foreground is part of the hydraulic apparatus for turning the converter upon its axis.

Fig. 94. Bessemer converter pouring finished molten steel into its proper ladle; from the ladle, molten steel is flowing to the ingot mold below.

The working of the Bessemer process is about as follows:

— Cast iron is melted in its furnace.

— Spiegel is melted in its furnace.

— Light fuel, such as kindling wood and afterward larger pieces of wood, is introduced into the converter, and set on fire to warm it. Next, the converter is turned upon its side. A charge of melted cast iron is then poured in. The air blast is now turned on. It plays over the surface of the molten iron. Next, the converter is turned upon its axis so as to take an upright position. Now, the air blast, streaming in full force through the molten iron, not only agitates it violently but also burns the carbon. As soon as the whole of the carbon is removed, the metal has virtually become wrought iron.

— A certain charge of melted *spiegeleisen* is run into the converter. This adds the amount of carbon requisite to produce steel. A few minutes of additional blowing mixes the metal thoroughly.

— The converter is turned upon its trunnions and the melted steel is poured into a large ladle and thence into ingot molds.

— As soon as the metal has cooled sufficiently to admit of "handling," the mold is stripped from the red-hot ingot and the latter is ready to be submitted to the action of machinery, it may be, to turn it into steel rails — the form in which Bessemer steel is most largely used.

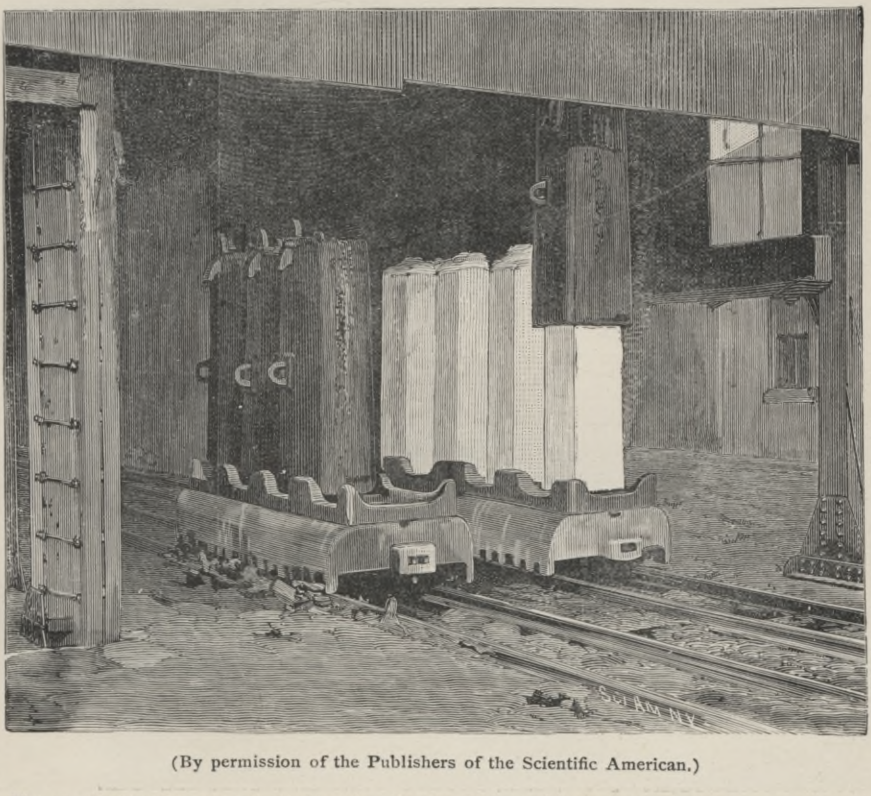

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Fig. 95. Ingot molds and hot steel ingots. On the right, machinery is "stripping" an ingot mold from its hot ingot.

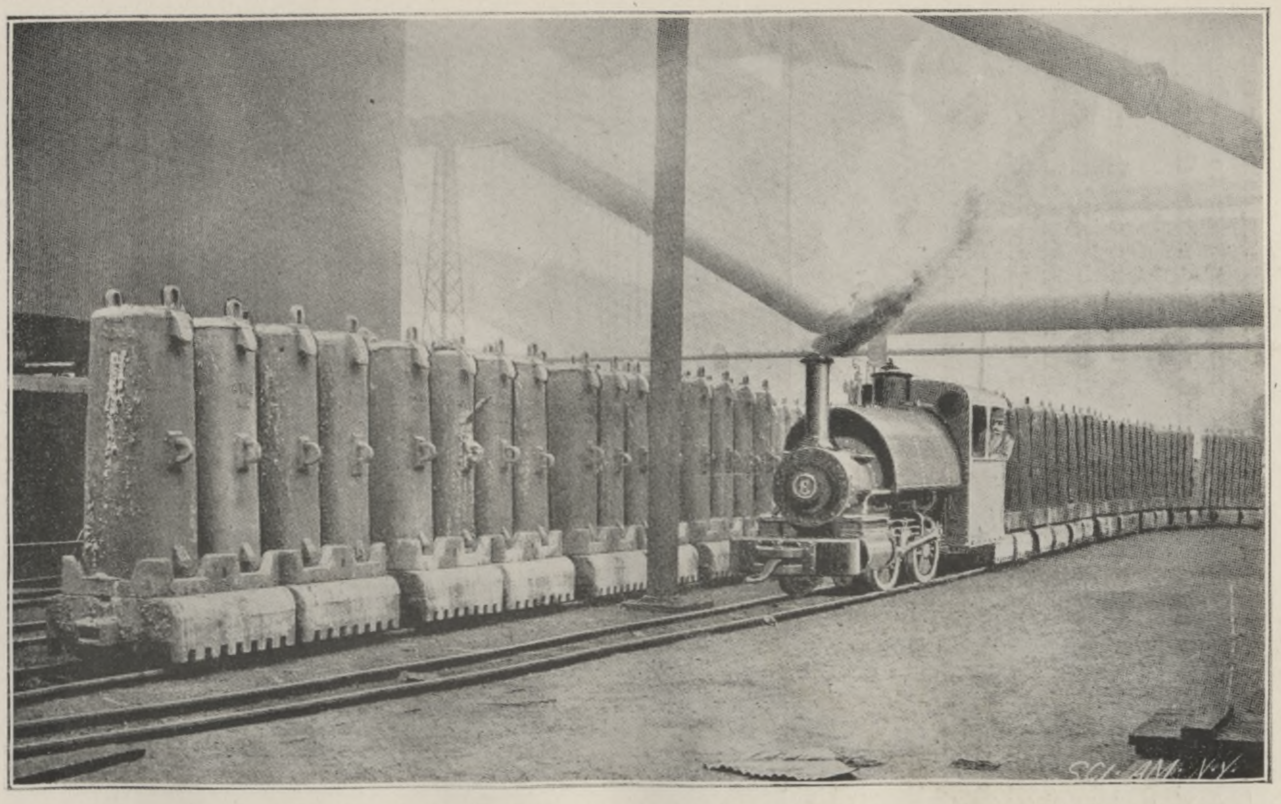

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Fig. 96. Train load of ingot molds containing steel ingots.

Comments on the Bessemer process. As an invention. Important and successful as the invention of Bessemer has become, there was a time, before it was perfected, when it seemed likely to fail. Its complete success, however, was partly due to a suggestion of Mr. R. F. Mushet: that of the addition of spiegeleisen at the end of the "blow."

Action of the blow. In the first five minutes of the Bessemer blow, the graphite is converted into combined carbon, the silicon and manganese are oxidized, as is a little iron. The latter give rise to a silicate of iron and manganese. When the last portions of carbon have been oxidized, the flame from the converter suddenly diminishes in amount. Now is the time to introduce the spiegeleisen or an equivalent amount of ferro-manganese. The duration of the blow varies from about fifteen minutes to about thirty minutes.

The converter lining. Bessemer's first lining was made of an earthy material called "ganister" composed mainly of silicon dioxide, an *acid* anhydride. With pig-iron containing phosphorus, Bessemer could not, at first, make good steel.

At length Messrs. Thomas and Gilchrist invented the use of a lining made chiefly of lime, a *basic* anhydride. Such a material promptly withdraws the phosphorus pentoxide, an *acid* anhydride produced by the blow — forming calcium phosphate, which is from time to time removed from the converter, as a slag now well-known as "Thomas slag." (The slag referred to is produced in such large quantities that it is employed as a source of phosphorus for commercial fertilizers.)

This *basic process* — simple as it appears — is deemed an invention second in importance only to the Bessemer process itself.

The Siemens-Martin (Open-hearth) Process for Steel Making.

The original invention of Charles William Siemens contemplated making steel, in a sense directly from iron ore. The original plan was to heat cast iron with natural oxide of iron — then the *oxygen* of the ore would burn out a part of the carbon of the cast iron, while the *iron* of the ore would blend with the iron of the cast iron.

The process was modified by Martin — the proposition being to produce steel by heating cast iron and wrought iron together.

Sir Charles William Siemens, inventor of the Siemens method of producing steel. (b. 1823, d. 1883.)

In this condition, instead of *absolutely* reducing the amount of carbon of cast iron (as in the Bessemer process), it is *relatively* reduced, — for the cast iron has more carbon, and the wrought iron less carbon, than has steel.

The process has been submitted in some places to yet other modifications, learned by the various forms of the Bessemer process — such as addition of *spiegel*, when required; moreover, the furnace has been supplied with a *basic* lining when phosphorus bearing irons are used.

The prime features of the method are at least three: *first*, the use of a furnace of reverberatory form (spoken of as the open-hearth); *second*, the use of gaseous fuel (producer gas); *third*, the use of the highly important *Siemens regenerators*, for heating the gaseous fuel before its combustion.

— *The materials used* may vary widely as stated already; but from what has been said it is plain that the output of steel is relatively large; moreover, when natural ores are used, an important economy of operation is secured.

— *The gaseous fuel*, called "producer gas," is a mixture of hydrogen and carbon monoxide, formed by driving superheated steam through red-hot coke. This gaseous fuel preserves the metal from contamination with ashes, and other impurities, introduced when solid fuel, like coal, comes in contact with molten metal.

— *The regenerative system* not only accomplishes a most important economy of fuel — it makes it possible to apply to the charges extremely high and well-controlled temperatures. It is operated in a manner somewhat similar to the Cowper "stoves" (already referred to under the Blast furnace).

The regenerative system involves the use of at least two sets of air chambers. The combustion of the gaseous fuel which has been heating the iron on the hearth, produces waste gaseous products which would ordinarily be *sent hot to the chimney*. In the Siemens process, they are directed into regenerative chamber A, and later to the chimney; but, being very hot, they raise the bricks in the chamber nearly to the white heat. Presently, by shifting a valve, the products are directed into regenerative chamber B, thus raising the temperature of the bricks there. Meanwhile, the same valve that has turned the waste gases into chamber B has admitted the fuel gases into chamber A. Thus, these latter are highly heated before they come into the reverberatory portion of the furnace; being *hot before they are burned*, they are in a condition to produce much more economical heating of the charge in the reverberatory.

Impurities in steel. The presence of phosphorus in steel is very objectionable. Steel containing .5 per cent. of carbon, should not contain more than .04 per cent. of phosphorus; otherwise it will not roll well.

A very minute quantity of silicon may improve steel. If slightly increased, however, it is injurious. Manganese, chromium, tungsten, titanium, copper, and perhaps other elements are sometimes present in steel. Generally speaking, the amounts of these substances should be small, unless, indeed, the steel is intended for some exceptional use requiring peculiar properties which may be imparted by one or more of these elements.

Steel is brought into the shapes desired, either by casting or by forging — the special kind of forging being oftenest conducted by passing red-hot ingots of the steel between powerful rolls. These rolls are so formed as to shape the steel mass before it cools. Railroad bars called rails are shaped in this way.

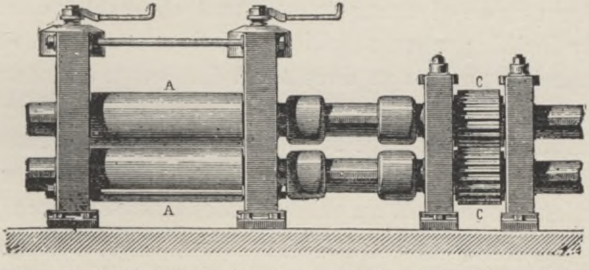

Fig. 98. "Rolls," for forming iron or steel ingots into bars or plates.

Alfred Krupp (deceased), German steel manufacturer, and owner of the great iron and steel works at Essen, Prussia.

Properties of Iron.

Iron, when practically pure, is white, lustrous, malleable and ductile.

Wrought iron approximates to pure iron (but it always contains recognizable amounts of other substances which modify its properties). It manifests the malleability of pure iron.

The various kinds of *steel*, which are, practically speaking, carbides of iron, differ much from pure iron. They are able to undergo remarkable and valuable changes of physical properties under the influence of the "tempering process," i. e , when heated, and then suddenly cooled.

The various kinds of *cast iron* are, practically speaking, higher carbides than steel. The physical properties of cast iron are different from those of wrought iron and of steel. Cast iron is more easily fusible ; when solid it is brittle ; it does not respond to the tempering process as does steel (although it does undergo a hardening change by the analogous process of "chilling").

All these forms of iron are strongly attracted by the magnet — more so than any other metal. (Only nickel, of the other metals, manifests this property in an easily demonstrated degree.)

A very large number of chemical compounds of iron has been recognized. Of these, there are at least *four well-defined series :* the *ferrous* compounds, in which the metal acts as a dyad, typical formula, $FeCl_2$; the *ferric* compounds, in which the metal acts as a pseudo-triad, typical formula, Fe_2Cl_6; the *ferrites* in which ferric oxide, Fe_2O_3, forms a variety of salts by combining with oxides like potassium oxide, K_2O; the *ferrates*, in which the theoretical ferric anhydride, FeO_3, combines with oxides like potassium oxide, K_2O.

A Few Compounds of Iron.

With fluorine;	Ferrous fluoride,	FeF_2		
	Ferric ———	Fe_2F_6		
With chlorine;	Ferrous chloride,	$FeCl_2$		
	Ferric ———	Fe_2Cl_6		
With bromine;	Ferrous bromide,	$FeBr_2$		
	Ferric ———	Fe_2Br_6		
With iodine;	(Iodides; composition doubtful)			
With oxygen;	Ferrous oxide,	FeO;	Ferrous hydroxide,	FeO_2H_2
	Ferric ———	Fe_2O_3;	Ferric ———	$Fe_2O_6H_6$
	Ferrosoferric ———	Fe_3O_4;	(another hydroxide)	
	(Ferric anhydride,	FeO_3?);	Ferric acid,	H_2FeO_4
			Potassium ferrate,	K_2FeO_4
With sulphur;	Ferrous sulphide,	FeS;	Ferrous sulphite,	$FeSO_3$
	Ferric ———	Fe_2S_3;	——— sulphate,	$FeSO_4$
	Iron ———	FeS_2;	Ferric sulphate,	$Fe_2(SO_4)_3$
	Ferrosoferric ———	Fe_3S_4;	(many other sulphates)	
With selenium;	Ferrous selenide,	$FeSe$		
With nitrogen;	(a nitride)		Ferrous nitrate,	$Fe(NO_3)_2$
			(many other nitrates)	
With phosphorus;	(several phosphides);		Ferric phosphate,	$FePO_4$
With carbon;	(Carbides like cast iron, etc.);		Ferrous carbonate,	Fe_2CO_3
	———	Fe_4C		
	———	FeC_2		
	———	FeC_3		
	———	FeC		

Ferrous hydroxide. FeO_2H_2, when prepared in the state of purity, is a white precipitate. It may be produced by adding an alkali to a solution of pure ferrous salt, great care being taken to exclude atmospheric air. It readily absorbs oxygen from the air or from the small amount of oxygen contained dissolved in water.

If a solution of pure ferrous salt in water has potassium hydroxide added to it, a greenish precipitate appears containing considerable ferrous hydroxide. The oxygen of the air quickly reddens it upon the surface, owing to the formation of ferric hydroxide.

Ferric oxide, Fe_2O_3, is a reddish powder. It may be produced by heating certain salts of iron so as to expel other acid radicles.

Thus, if ferrous sulphate is heated, water of crystallization and a part of the sulphuric acid radicle are expelled and a reddish ferric oxide appears. This substance is somewhat employed as a pigment. It is also used as a polishing powder. When mixed with soap or stirred into paraffin wax, a reddish solid is produced which may be employed for cleaning brass and similar uses.

Ferric hydroxide, $Fe_2O_6H_6$, appears as a reddish flocculent precipitate when an alkali is added to a ferric solution. This red substance is practically the same as the iron rust produced by exposure of iron to air and moisture.

Ferroso-ferric oxide, Fe_3O_4, often called magnetic oxide, is a black solid produced when iron is heated to redness in the air. By striking the iron with a hammer, solid flakes of the oxide fall off, whence the material is often called iron scales.

Ferroso-ferric oxide is also produced when steam is passed over red-hot iron turnings.

Ferroso-ferric oxide is produced in a hydrated form when an alkali is added to a solution containing in proper proportions a mixture of ferrous and ferric compounds. The black precipitate, which thus falls in the water is magnetic — as may be shown by applying a magnet to the outside of a beaker containing it.

Potassium ferrate is a reddish solid produced when oxides of iron are heated with potassium nitrate or potassium hydroxide or both. The compound is unstable; that is, it easily decomposes.

Ferrous sulphate, called copperas or green vitriol, $FeSO_4 \cdot 7H_2O$, is a green crystalline salt formed by dissolving iron in sulphuric acid. In "pickling" iron wire or iron castings, large quantities of this salt are produced.

Certain iron pyrites, when gently roasted in heaps, oxidize, changing from FeS_2 to $FeSO_4$. When the ashes are treated with water, the ferrous sulphate dissolves and may afterwards be obtained in crystals. Large quantities of copperas are produced in this way.

Copperas, or green vitriol, is largely employed as a mordant in the dyeing and coloring of cotton and woolen goods. With dye-stuffs, under proper conditions, it produces black colors. It is used in connection with nutgalls (which contain tannin) to produce writing ink. It is largely employed in the preparation of Prussian blue, which substance is used in the laundry as "blueing," and for many purposes where a dark blue pigment is desired, in calico printing, for example. Ferrous sulphate is also employed in calico printing to produce what is known as iron buff. In this case, however, the iron is precipitated upon the cloth in the form of ferrous hydroxide, which by oxidation is subsequently changed to ferric hydroxide and thence to ferric oxide.

Prussian blue is a name applied in a general way to certain deep blue compounds produced by combinations of iron with one or the other of two compound radicles called respectively ferrocyanogen and ferricyanogen.

Cyanogen is a compound of carbon and nitrogen having the formula CN. It is known as a colorless gas composed of two groups of the cyanogen radicle, cyanogen gas being expressed by the formula CN.CN. Cyanogen has a remarkable power of combining with certain metals to form more complex radicles. Thus, it produces hydroferrocyanic acid, $H_4(CN)_6Fe$. It also produces hydroferricyanic acid, $H_3(CN)_6Fe$. These substances produce salts of potassium, named respectively, potassium ferrocyanide, called yellow prussiate of potash, $K_4(CN)_6Fe$), and potassium ferricyanide, called also red prussiate of potash, $K_3(CN)_6Fe$.

When potassium *ferrocyanide* is added to a solution of a *ferric* salt, a deep blue precipitate is produced, commonly called Prussian blue. It is not strictly ferric ferrocyanide. It always contains some potassium compounds as well. It is sometimes known as Williamson's blue.

When potassium *ferricyanide* is added to a solution of *ferrous* sulphate, a deep blue precipitate is produced, called Turnbull's blue. It has approximately the composition suggested by the name ferrous ferricyanide; but it is even more complex, always containing some potassium compounds.

NICKEL; Ni; 58, 69.

Data for Reference.

Density of solid nickel, 8.97 (water being the standard = 1).

Fusing point of solid nickel, 1400°—1420° C.

Metallic nickel was isolated first by Cronstedt, in 1754.

The word nickel is derived from the German name of an ore of nickel, *Kupfernickel*, false copper.

The mediæval metallurgists were unable to extract metallic nickel from its ores; yet the Chinese have used *alloys of nickel* for ages.

Nickel occurs in the earth in a certain rare alloy with platinum. (Nickel generally exists in meteorites.)

The principal ores of nickel are the following:

Kupfer nickel,	nickel arsenide,	Ni_2As_2
White nickel,	nickel arsenide,	$NiAs$
Millerite, or nickel blende,	nickelous sulphide,	NiS
Garnierite,	magnesium nickel silicate,	$2(NiMg)_5Si_4O_3 \cdot 3H_2O$.

The last mentioned mineral, found in New Caledonia, contains large quantities of nickel, and, contrary to the ordinary experience, is free from cobalt — a manifest advantage.

The general principles upon which metallic nickel is produced are the same as those employed for obtaining iron, cobalt, and many similar metals. Owing to the rarity of nickel ores, however, it becomes necessary to employ those which contain not only small quantities of nickel but considerable quantities of other metals. By the ordinary processes these would be reduced to the metallic form at the same time, thus yielding *alloys of nickel*, instead of the pure metal sought. On this account the preparation of the pure metal is difficult.

1 — The preparation of nickel usually involves a combination of a series of dry processes and wet processes.

The dry processes involve roastings to accomplish the expulsion of certain volatile substances, like sulphur and arsenic.

The wet processes secure the removal of metals like cobalt, copper, iron, etc. At the same time, they bring the nickel to the form of oxide. The production of this oxide is the step preceding the final preparation of nickel.

The oxide is pressed into cubes ; it is then heated in crucibles containing powdered charcoal ; thus is produced metallic nickel in the form called *cube nickel.* The nickel may be subsequently heated and rolled into plates.

2 — Mond's process depends upon the formation of a gaseous compound of nickel, nickel carbon oxide, $Ni(CO)_4$. When this is accomplished the nickel is, as it were, evaporated out of the ore, leaving all impurities behind. Subsequently the nickel is easily separated from the gas.* (See p. 262.)

Nickel is a hard, white metal having a peculiar well-known color, possessing darker reflections than silver. It does not oxidize readily in water, nor does it tarnish from presence of sulphuretted hydrogen, or similar gases in the atmosphere, which tarnish silver articles. Nickel is distinctly magnetic, though less so than iron.

The two chief uses of nickel in the arts are first, in the manufacture of alloys; and, second, in the processes of electroplating.

A Few Compounds Containing Nickel.

With fluorine ;	Nickelous fluoride,	NiF_2		
With bromine ;	—— bromide,	$NiBr_2$		
With chlorine ;	—— chloride,	$NiCl_2$		
With iodine ;	—— iodide,	NiI_2		
With oxygen ;	Nickelous oxide,	NiO		
		Ni_3O_4		
	Nickelic oxide.	Ni_2O_3		
With sulphur ;		Ni_2S ;	Nickelous sulphite,	$NiSO_3$
	Nickelous sulphide,	NiS ;	—— sulphate,	$NiSO_4$
		Ni_3S_4		
		NiS_2		
With nitrogen ;			Nickelous nitrate,	$Ni(NO_2)_2$
			—— nitrate,	$Ni(NO_3)_2$
With phosphorus :		Ni_5P_2 ;	—— phosphate,	$Ni_3(PO_4)_2$
		Ni_2P		
		Ni_3P_2		
With carbon ;	Nickel carbon oxide,	$Ni(CO)_4$,	Nickelous carbonate,	$NiCO_3$
With silicon ;	Nickelous silico-fluoride,	$NiSiF_6$		

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* *Chem. News*, 78 : 260.

Nickel carbon-oxide, $Ni(CO)_4$, a gas, is the first gaseous compound of nickel discovered. It was produced (about 1890) by Mond, Langer, and Quincke, by *first* reducing a compound of nickel to the metallic form (in a finely divided state), by *second* passing carbon monoxide over the nickel while moderately heated (to about 100° C.). By this process the carbon monoxide takes up the nickel and carries it off in the form of the gaseous compound under consideration.

The gas may be liquefied. It is soluble in benzine, in petroleum, and certain other similar oils. When the gas is heated to 150° C., it is thermolyzed with deposition of its nickel. The gas easily burns in the air. Mond has established an experimental working plant for extracting nickel from its impure ores, by ingenious use of the facts stated above.

COBALT; Co; 58, 93.

Data for Reference.

Density of solid cobalt, 8.5 — 8.9 (water being the standard = 1).

Fusing point of solid cobalt, about 1500° C.

Cobalt was recognized as an element by Brandt in 1735

The name cobalt is supposed to be derived from the German word *Kobold*, a goblin. (The suggestion relates to the ideas of the mediæval metallurgists with respect to heavy ores from which they could not extract any metal.

Cobalt compounds have been used, from very early times, for coloring glass blue.

Cobalt and nickel are very closely related, as their similar atomic weights and specific gravities at once suggest; moreover, they are often found associated in ores in the earth. (It is not absolutely certain that cobalt and nickel are elements.*)

Cobalt occurs in some meteorites.

Cobalt is found in a large number of minerals (though in small quantities in most of them). The following may be mentioned:

Smaltine, chiefly cobalt arsenide, $CoAs_2$;
Cobalt glance, arsenio-sulphide of cobalt, $CoAsS$;
Linnaeite, cobalt sulphide, Co_3S.

In preparing metallic cobalt, the chief difficulty arises in the need of separating other elements existing in the ore of cobalt: as arsenic, copper, lead, iron. These are usually separated by certain wet processes whereby eventually an oxide of cobalt is obtained; and this oxide is finally reduced by a dry process, that is, by heating it with the reducing agent in a crucible or other piece of apparatus.

Metallic cobalt bears a considerable resemblance to metallic nickel. It is bright and lustrous, has a whitish color; it is somewhat magnetic, as nickel is. Chemically also it resembles nickel in the types of its compounds, though not in the colors of them. (Cobalt compounds *tend* toward pink shades of color, while nickel compounds *tend* toward green.)

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* *Supposed decomposition of cobalt and nickel.*—Kruss and Schmidt, while studying cobalt and nickel for the purpose of re-estimating their atomic weight, have obtained certain results which lead them to the opinion that they have proved these so-called elements to be in fact compounds. *Chem. News*, *59: 64*.

(Also *Am. Ch. J.*, *11:121*.)

Fleitman controverts this. *Chem. News*, *60: 9*.

Cobalt has been used to some extent in the process of electro-deposition. When thus deposited the eye does not readily distinguish it from electro-deposited nickel.

A Few Compounds Containing Cobalt.

With fluorine;	cobaltous fluoride,	CoF_2		
With chlorine;	——— chloride,	$CoCl_2$		
With bromine;	——— bromide,	$CoBr_2$		
With iodine;	——— iodide,	CoI_2		
With oxygen;	Cobalt monoxide,	CoO;	Cobaltous hydroxide,	CoO_2H_2
	Cobaltous-cobaltic oxide,	Co_3O_4		
	Cobaltic oxide,	Co_2O_3;	Cobaltic hydroxide,	$Co_2O_6H_6$
		Co_4O_5		
		Co_5O_6		
		Co_6O_7		
		Co_8O_9		
With sulphur;		Co_4S_3;	Cobaltous sulphite,	$CoSO_3$
	Cobaltous sulphide,	CoS;	——— sulphate,	$CoSO_4$
		Co_3S_4;	Cobaltic ———	$Co_2(SO_4)_3$
		Co_2S_3		
		CoS_2		
With nitrogen;	(an immense number of complex ammonium compounds.)		Cobaltous nitrate,	$Co(NO_3)_2$
With phosphorus,		Co_3P_2		
With carbon;			Cobaltous carbonate,	$CoCO_3$
			——— sodium ———	$CoNa_2(CO_3)_2$

Cobalt forms a great many ammonium substitution compounds. The statement, below, of the recognized series, affords a suggestion of their number and complexity. Speaking generally, cobalt compounds may absorb or unite with ammonia gas, and then the combination may combine with acid radicles in a great variety of ways to produce the new compounds called cobaltamines, or the cobalt ammonium bases, or by other names:

Class 1 — Cobaltamines.

These may be represented by the general formula, $M \cdot xNH_3$, in which M represents a cobalt salt, and x has generally the value 6. Example, $CoCl_2 \cdot 6NH_3$.

Class 2 — Oxycobaltamines.

General formulas; $Co_2(NH_3)_{10}R_4OHOOH$ and $Co_2(NH_3)_{10}R_5OOH$, in which R represents an appropriate acid radicle.

Class 3 — Cobaltiamines.

Series i — Hexamines —	$Co_2(NH_3)_6R_6$.	
Series ii — Octamines —	$Co_2(NH_3)_8R_6$	Praseo cobaltic salts Fusco cobaltic " Croceo cobaltic "
Series iii — Decamines —	$Co_2(NH_3)_{10}R_6$	Roseo cobaltic " Purpureo cobaltic " Xantho cobaltic "
Series iv — Dodecamines —	$Co_2(NH_3)_{12}R_6$	Luteo cobaltic "

Cobaltous nitrate, $Co(NO_3)_2 \cdot 6H_2O$, is a red crystalline salt, the commonest salt of cobalt used by the chemist.

Smalt is a pulverized blue glass colored with oxide of cobalt. It is used for various coloring purposes, as in certain oil paints, and in the blueing of the starch applied to certain cotton fabrics.

Cobalt and its compounds have very few uses in the arts. The largest field for the consumption of cobalt is the glass manufacture. A small amount of oxide of cobalt gives an exceedingly deep blue color to glass; and most blue glass is colored by cobalt compounds.

RUTHENIUM; Ru; 101, 68.

Data for Reference.

Density of solid ruthenium, 12.26 (water being the standard = 1).

Ruthenium fuses only at as high temperatures as that of the compound blow pipe, about 2000° C.

Ruthenium was proposed by Osann, in 1828; Claus, in 1845, obtained the metal now accepted.

The word ruthenium is derived from the Latin word *Ruthenia*, Russia.

Ruthenium is found in platinum ores, espccially in that called osmiridium.

Ruthenium may be prepared by reducing certain of its compounds, by heating in a current of hydrogen gas. (But it is by no means easy to prepare the initial compound in a state of purity.)

Ruthenium is a white, hard, heavy, brittle metal. It forms compounds of a type similar to those of other platinum metals. Thus it forms the chlorides $RuCl_2$, $RuCl_3$; the oxides, RuO, Ru_2O_3, RuO_2, RuO_4 (and perhaps others); the sulphate, $Ru(SO_4)_2$; many ruthenates of the general formula M_2RuO_4; and many other known compounds.

Like several of the platinum metals it forms many complex ammonium substitution compounds. These have been arranged in series (as have those of rhodium, and chromium, and cobalt).

i — Hydroxy-compounds,	general formula,	$OH{\cdot}NO{\cdot}Ru(NH_3{\cdot}NH_3R)_2$
ii — Chloro-compounds,		$Cl{\cdot}NO{\cdot}Ru(NH_3{\cdot}NH_3R)_2$
iii — Nitrato-compounds,		$NO_3{\cdot}NO{\cdot}Ru(NH_3{\cdot}NH_3R)_2$
iv — Sulphato-compounds,		$SO_4 2[NO{\cdot}Ru(NH_3{\cdot}NH_3R)_2]$

(In these general formulas R represents a variety of electro-negative radicles.)

RHODIUM; Rh; 103, 01.

Data for Reference.

Density of solid rhodium, 12.1 (water being the standard = 1).

Fusing point of solid rhodium, about 2000° C.

Rhodium was discovered by W. H. Wollaston in 1803.

The word rhodium is derived from a Greek word ῥόδον *(rhodon)* a rose. The name was suggested by the red color of the salts of the metal.

Rhodium is found in the earth alloyed with the other metals of the second and third sections of this group (the platinum metals) in the ordinary ore of platinum.

The metal may be prepared by reducing certain salts of rhodium in a current of hydrogen. (But it is by no means easy to prepare the pure salt, because the metals associated with rhodium in platinum ore are very similar in their chemical reactions.)

Rhodium is a white, hard, heavy, ductile, malleable metal, It forms compounds of a type similar to those of the other platinum metals. Thus it forms the chloride $RhCl_3$ (and perhaps others); the oxides RhO, Rh_2O_3, RhO_2; the sulphate $Rh_2(SO_4)_3$, etc.

Like several of the platinum metals rhodium forms many complex ammonium substitution compounds. These have been arranged in three principal groups (compare chromium and cobalt complex ammonium compounds):

i — Purpureo-rhodium compounds,	general formula,	$M_2Rh_2\cdot 10NH_3\cdot X_4$
ii — Roseo-rhodium	———	———	$Rh_2\cdot 10NH_3X_6\cdot 2H_2O$
iii — Luteo-rhodium	———	———	$Rh_2\cdot 12NH_3X_6$

(In these general formulas, M and X represent electro-negative radicles; in a given case they may be alike or different.)

PALLADIUM; Pd; 106, 36.

Data for Reference.

Density of solid palladium, 11.4 (water being the standard = 1).

Fusing point of solid palladium, between 1360° and 1500° C.

At 2000° C. palladium changes to vapor.

Palladium was discovered by W. H. Wollaston in 1803.

The name Palladium is derived from the name of the planet Pallas (discovered a short time before the metal was recognized).

Palladium exists in the earth in the complex alloy constituting platinum ore. It exists occasionally in certain forms of native gold.

Palladium has been prepared by several methods e. g., by heating the compound, palladium cyanide, $Pd(CN)_2$.

Palladium is a white, hard, heavy, malleable and ductile metal. The metal has to a remarkable degree the power of absorbing gases, especially hydrogen gas, by the process called occlusion.

Palladium forms compounds of types similar to those of other platinum metals. Thus, it forms the chlorides, $PdCl$, $PdCl_2$, (and $PdCl_4$, in combinations); the oxides, Pd_2O, PdO, PdO_2; the sulphate, $PdSO_4$; and many others. Its iodide, PdI_2, is a black precipitate (whence palladium salts are used in the quantitative separations of iodine).

Like several of the platinum metals palladium forms a large number of complex ammonium substitution compounds. They have been arranged in two series:

I — Pallados diammonium compounds, type compound, $Pd(NH_3.NH_3)Cl_2$
II — Ammonium pallados-diammonium compounds, —— $Pd(NH_2NH_4.NH_2NH_4)Cl_2$

In the two series mentioned there is known to exist a considerable opportunity for replacing Cl_2 by other appropriate electronegative radicles.

The physical properties of palladium are such as fit it for a certain variety of uses in the arts; thus it is employed on the graduated scales of certain optical instruments, in which case it affords white and non-corroding surfaces. But its rarity makes it very costly — more so than even platinum.

OSMIUM; Os; 190, 99.

Data for Reference.

Density of solid osmium 22.477 (water being the standard = 1).

Osmium does not fuse at the highest temperatures of the compound blowpipe flame (estimated at about 2000° C.)

Osmium was discovered by Tennant, in 1804.

The word osmium is derived from the Greek word ὀσμή (*osme*) odor. (The reference is to a peculiar odor possessed by a compound of the metal.)

The metal osmium is found in the earth alloyed with other metals of its group, in the chief ore of platinum. When this ore is treated with aqua regia, certain of the metals dissolve; but there remains an undissolved part called osmiridium (containing from 27 per cent. to 45 per cent. of osmium).

Osmium may be prepared from certain of its compounds, by several methods, e. g., by heating them in an atmosphere of hydrogen.

Osmium compounds are obtained from the insoluble residues remaining after platinum ores have been treated with aqua regia.

Osmium is a white, heavy, hard, very difficultly fusible metal. It forms compounds of a type similar to those of other platinum metals. Thus it forms the chlorides, $OsCl_2$, $OsCl_4$; the oxides OsO, Os_2O_3, OsO_2, OsO_4 (the latter may well be called perosmic anhydride, though formerly called osmic acid and perosmic acid). No *true* osmic acid is known, but osmates of the type of K_2OsO_4, are known (and perosmates are anticipated).

Osmium, like several other platinum metals, forms many complex ammonium substitution compounds. The molecular structure of these compounds has not yet been well made out, but it seems that they may be looked upon as of two groups — in one of them, two molecules of NH_4 have hydrogen replaced by the radicle, OsO; in the other, two molecules of NH_4 have hydrogen replaced by the radicle, OsO_2.

Osmium tetroxide, OsO_4 (formerly called osmic acid) may be produced by heating osmium in oxygen. It is a solid which easily melts, and easily volatilizes affording a vapor which is very offensive in odor and very poisonous; it has a powerfully oxidizing influence on animal and vegetable substances.

IRIDIUM; Ir; 193, 12.

Data for Reference.

Density of solid iridium 22.42 (water being the standard = 1).
Fusing point of solid iridium, cannot be stated (it is certainly very high).
Iridium was discovered by Tennant, in 1804.
The name iridium is derived from a Greek word, ἶρις (*iris*) the rainbow.

The metal iridium is found in the earth, alloyed with other platinum metals, in platinum ores.

The metal may be produced by decomposing certain of its compounds, as ammonio-iridic chloride, $(NH_4)_2IrCl_6$, by heating.

Iridium is an extremely hard, heavy, white, difficultly fusible metal.

It forms compounds of a type similar to those of the other metals of its section. Thus it forms the chloride, $IrCl_3$ (and by analogy $IrCl_4$, in combination, in double salts) ; the oxides, Ir_2O_3, IrO_2.

Iridium, like the other platinum metals forms a number of complex ammonium substitution compounds. But fewer compounds of iridium of this class are known than in case of most of the other metals of the platinum group.

Considerable quantities of iridium are obtained incidental to the manufacture of platinum.

It has been proposed to use an alloy consisting of ninety per cent. platinum and ten per cent. pure iridium for the preparation of a standard metre measure for international purposes.

There are no considerable commercial uses for the metal iridium or its compounds.

PLATINUM; Pt; 194, 89.

Data for Reference.

Density of solid platinum, 21.5 (water being the standard = 1)
Fusing point of solid platinum, about 1775° C.

In 1741, Watson received a metal-like substance from the bed of the river Pinto in New Grenada; it was called *platina del Pinto;* from it he separated the new metal and called it platinum.

The word platinum is derived from the Spanish word *platina*, supposed to be a diminutive of the Spanish word *plata*, silver.

Platinum is found in the earth in the ore called native platinum, an alloy containing from 60 per cent. to 86 per cent. of platinum. (The balance is made up of from 5 per cent. to 10 per cent. of iron and copper, with smaller quantities of the other metals of the platinum group.)

The most important sources of the ore are the placers of the Ural mountains at a few points located at about 60° E., 58° N. The sands and gravels are washed in crude sluices, and then the rich concentrates, containing the ore in the form of scales and rounded particles, are sent out of the country to be refined (largely by Johnson, Matthey & Co. of London) *

In refining, the crude ore is treated with aqua regia, which dissolves the platinum ; the excess of acid is removed by evaporation; the residue is dissolved in water and filtered; to the clear filtrate, ammonium chloride is added — now the platinum forms a precipitate of ammonio-platinic chloride, $(NH_4)_2PtCl_6$. This precipitate is heated so as to expel ammonium chloride and chlorine, and leave the platinum in a spongy form. This sponge is fused in a crucible of lime, under the flame of the compound blowpipe.

The scientific uses of platinum are very important, although it may be admitted perhaps that the range of uses is somewhat narrow. Platinum dishes and crucibles, platinum wire and foil, are of the first moment to the chemist. Liebig long ago declared that "without platinum, the composition of most minerals would have yet remained unknown."

Again, platinum in solution is extremely valuable as a reagent for precipitating potassium and ammonium and many substances of complex composition, such as animal and vegetable alkaloids, which are allied to ammonium in plan of structure.

In the arts, platinum is of great importance in three principal lines.

In the *manufacture of sulphuric acid*, platinum retorts are very important. In the manufacture of *incandescent electric lamps*, wires of platinum convey the current through the air-tight glass walls of the bulb. (No substance has yet been discovered that will satisfactorily take its place in this field.) In the Welsbach

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* *The Mineral Industry*, 6: 539.

incandescent gas burner, the mantle (see p. 194) is often held in place by a short piece of platinum wire.

The most important *physical properties* of platinum are its bright white color which it retains without tarnishing; its difficult fusibility; its power of being welded long before it reaches the melting point; its low conducting power for electricity; and its power of occluding hydrogen and other gases. Its chief *chemical properties* are its resistance to agents other than aqua regia* (or its equivalent) and its tendency to form double compounds with potassium, ammonium, and many vegetable and animal alkaloids, capable of classification with ammonia.

A Few Compounds Containing Platinum.

(Discriminate between the platinous or platino, on the one hand, and the platinic or platini, compounds, on the other.)

With hydrogen;	(hydrides probably exist)	
With fluorine;	Platinic fluoride, PtF_4	
With chlorine;	Platinous chloride, $PtCl_2$;	Platino chlorohydric acid, H_2PtCl_4
		Potassium platino chloride, K_2PtCl_4
		Ammonium ——— ——— $(NH_4)_2PtCl_4$
	Platinic ——— $PtCl_4$;	Platini chlorohydric acid, H_2PtCl_6
		Potassium platini chloride, K_2PtCl_6
		Sodium ——— ——— Na_2PtCl_6
		Ammonium ——— ——— $(NH_4)_2PtCl_6$
With bromine;	Platinous bromide, $PtBr_2$;	Platino bromohydric acid, H_2PtBr_4
		Potassium platino bromide, K_2PtBr_4
	Platinic ——— $PtBr_4$;	Platini bromohydric acid, H_2PtBr_6
		Potassium platini bromide, K_2PtBr_6
With iodine;	Platinous iodide (probably), PtI_2;	Platino idohydric acid, H_2PtI_4
	Platinic ——— PtI_4;	Platini ——— ——— H_2PtI_6

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* But in certain cases of alloys containing silver and platinum, when the silver is dissolved in nitric acid, the platinum dissolves with it.

With oxygen;	Platinous oxide,	PtO;	Platinous hydroxide,	PtO_2H_2
	Platinum tetroxide,	Pt_3O_4		
	Platinic oxide,	PtO_2;	Platinic ———	PtO_4H_4
			Sodium platinate,	$Na_2O \cdot 3PtO_2$
			Barium ———	$3BaO \cdot 2PtO_2$
With sulphur;	Platinous sulphide,	PtS;	Platinous sulphate,	$PtSO_4$
	Platinum sesquisulphide (?),	Pt_2S_3;	Thio platinous acid,	H_2PtS_4
	Platinic sulphide,	PtS_2;	Platinic acid,	$Pt(SO_4)_2$
			Thio platinic acid,	H_2PtS_6
With nitrogen;			(many ammonium substitution compounds. See text.)	

In addition to the compounds above mentioned, platinum forms many others. But special attention should be directed to those numerous and complex ammonium substitution compounds of platinum analogous to the groups of this general character already referred to in connection with the other platinum metals (and with cobalt; see p. 264).

Ammonia gas and platinum compounds may unite to form certain groups called *ammoniacal platinum bases*, which may unite with basic or acid radicles, or both at once, to form a great number and variety of more complex salts. These compounds have been arranged in three classes and many sub-classes:

Class 1 — Platoso compounds

Series i — Platosemiammines,
Series ii — Platosammines,
Series iii — Platodiammines,
Series iv — Platosemidiammines,
Series v — Platomonodiammines.

Class 2 — Platini compounds.

Series i — Platinammines,
Series ii — Platinidiammines,
Series iii — Platinisemidiammines,
Series iv — Platinimonodiammines,
Series v — Platininitriammines.

Class 3 — Diplatinum compounds.

Series i — Diplatodiammines,
Series ii — Diplatosoindiammines,
Series iii — Diplatinammines,
Series iv — Diplatinidiammines.

Above one hundred compounds, capable of distribution in the series named have been produced already.

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