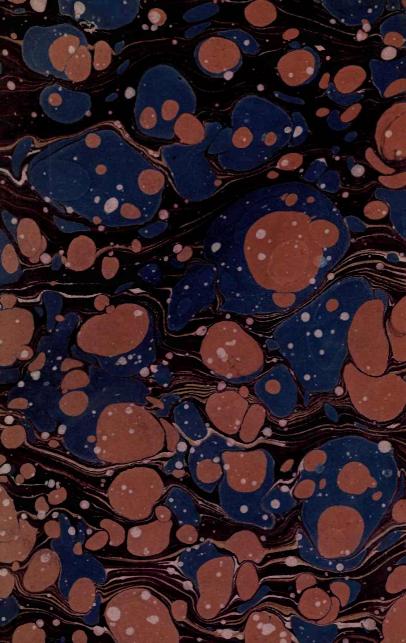
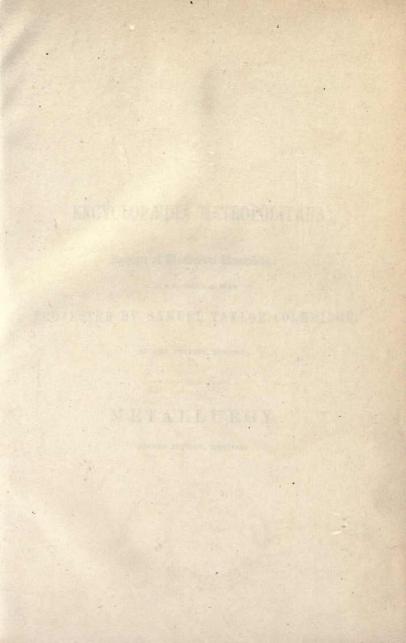


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# ENCYCLOPÆDIA METROPOLITANA:

OR

System of Anibersal Unowledge :

ON A METHODICAL PLAN

PROJECTED BY SAMUEL TAYLOR COLERIDGE.

SECOND EDITION, REVISED.

# METALLURGY.

SECOND EDITION, REVISED.

In preparation, uniform with this Volume,

289

## A MANUAL OF GEOLOGY,

PRACTICAL AND THEORETICAL.

BY JOHN PHILLIPS, M.A., F.R.S., F.G.S.,

DEPUTY READER IN GEOLOGY IN THE UNIVERSITY OF OXFORD.

Mith Rumerous Engrabings.

# MANUAL OF METALLURGY,

A

OR

# A PRACTICAL TREATISE

ON THE

# CHEMISTRY OF THE METALS.

## By JOHN ARTHUR PHILLIPS, F.C.S.

SECOND EDITION, REVISED.

Illustrated by Humerous Engrabings.

LONDON AND GLASGOW: RICHARD GRIFFIN AND COMPANY,

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1854.



### PREFACE TO THE FIRST EDITION.

THE methods of extracting the metals from their ores are so extremely varied that it would be impossible to comprise them all within the limits of a single volume; the more important processes have therefore been selected.

In describing these, the necessary facts have been presented to the student in the order in which a knowledge of them is required; the crude ores being traced from the mines in which they occur through the various mechanical and metallurgic elaborations which they subsequently undergo before the metal is obtained.

The student of metallurgy should be enabled to distinguish, by their crystallographic as well as by their chemical characters, all the more frequently occurring ores, and be familiarly acquainted with the composition and properties of the various fuels employed in furnace operations.

With a view to facilitate the acquirement of this knowledge, a short chapter on crystallography has been introduced, whilst another has been devoted to natural and artificial fuels. The information which has been given on the important subject of Assaying will, it is hoped, sufficiently supply a want which has been long felt in this country.

In the preparation of this volume, the works of Dufrenoy, Regnault, Berthier, Knapp, Scheerer, Le Play, Rammelsberg, Lampadius, Dana, Karsten, and Heron de Villefosse, have been consulted. Other authors whose works have been used will be found specially mentioned in the text.

As a former pupil of the first-named mineralogist, I have employed in a condensed form the system of crystallography adopted in his valuable work on that subject, from which have been taken the greater portion of the diagrams relating to the laws of crystallisation.

The other illustrations are either original, and have been drawn expressly for the present Treatise, or, when relating to foreign methods, have been adapted from French and German books in which the subjects are well represented.

8, UPPER STAMFORD-STREET, April, 1852.

## PREFACE TO THE SECOND EDITION.

THE rapidity with which the former Edition of the "Manual of Metallurgy" has been exhausted, sufficiently proves that such a treatise was required by those who are engaged in metal manufacture or mining operations.

In preparing the present Edition for the press, the original order of arrangement has been retained—since it has been found useful as a course for study, and easy as a system for reference.

The greatest attention has been devoted to this Edition, to ensure correctness in each scientific detail and manipulation, and in every practical result.

The process for the purification of Tin, and the European process of Amalgamation, are both new and important.

The object has been to render this Manual a useful standard of reference alike to the student and manufacturer.



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# METALLURGY.

### INTRODUCTION.

A KNOWLEDGE of the more common metals, and the means of extracting them from their ores, was probably coeval with the first formation of civil communities, and long prior to the invention of written characters, or any other method of transmitting to posterity the memory of past events; and we are consequently without information relative to the period at which mankind first commenced this species of industry, or the steps which first led to the discovery of a class of bodies now become so necessary to our daily wants.

We have, however, sufficient reasons for believing that the antediluvians were well acquainted with these arts, and that they were, in all probability, extensively practised at a very early period.

In the days of Moses, at least six metals were in common use, as they are distinctly mentioned as forming part of the spoils of the Midianites, who appear to have possessed them in considerable abundance.

Among the ancient Greeks and Romans, Metallurgy was cultivated to so great an extent, that many of their productions, although made at an infinitely greater expense of time and labour, are scarcely to be surpassed by the most skilful artists of the present day, aided by the numerous inventions of modern times.

Of the state of this science in Europe prior to the commencement of the sixteenth century, little is at present known; for although the metals were doubtless extracted in considerable quantities no books on the subject had yet appeared; and we are consequently more indebted for information to the various remains of ancient foundries which have been discovered, than to any written treatise. In the year 1530, Georgius Agricola, a German physician, published his twelve books *De Re Metallica*; and although one or two works on metals had already appeared in the German language, and one in Italian, he may justly be considered the first author who gave a clear and correct description of the various processes employed in this branch of chemical science.

Lazarus Erckern, Assay-Master-General to the empire of Germany, followed Agricola in the same pursuit, and in 1574 published a work at Prague, of which an English translation, by Sir John Pettus, came out in 1683. Since that time numerous treatises on this subject have appeared in almost every European language, and Metallurgy has rapidly risen to that prominent position among the useful arts which it holds at the present day.

The ancients were acquainted with seven metals, and these they designated by the names of the planets, and represented by symbols supposed to have some mysterious allusion to those bodies.

Gold wa	ıs	call	ed	the	Sun, and	$^{\rm th}$	us	rep	ores	ent	$\mathbf{ed}$				$\odot$
Silver					Moon			•							D
Mercury	T				Mercury										¥
Copper			•		Venus	•									Ŷ
Iron .	•	•			Mars .		•		•		•		•		8
Tin .	•		•	•	Jupiter	•	•			•	•		•		24
Lead	•		•	•	Saturn	•	•	•	•		•		•	•	ħ

Zinc, as a metal, was not anciently known, although advantage had been taken, some time prior to the Christian Era, of the property possessed by its ores of converting copper into brass (Quarterly Journal of the Chemical Society, October, 1851). Zinc is first mentioned by Paracelsus, who died in 1541. Bismuth is described in the Bermannus of Agricola, written about 1830. Antimony was discovered by Basil Valentine towards the close of the fifteenth century. Arsenic and Cobalt are first mentioned by Brandt in 1733 (Acta Upsal. 1733 and 1742); but their ores had been known long before. Platinum was first recognised as a new metal in 1741, by Charles Wood, Assay-Master in Jamaica (Phil. Trans. vol. xliv.) In 1751 Cronstedt showed that Nickel was a distinct body (Stockholm Trans). Manganese was first obtained by Ghan in 1774 (Bergman's Opuscula, vol. ii.); and Tungsten was discovered by M. Delhuyart in 1781 (Mémoires de Toulouse). Tellurim and Molybdenum by Müller and Hielm in 1782 (Crell's Annals, 1790 and 1798). Uranium by Klaproth in 1789. Titanium by Gregor in the same year (Journ. de Phys. xxxix.) Chromium by Vauquelin in 1797 (Ann. de Chimie, vol. xxv.) Columbium was discovered by Hatchett in 1802 (Phil. Trans.) Palladium and Rhodium were discovered by Wollaston, and Iridium and

Osmium by Tennant, in 1803 (Phil. Trans.) Cerium was announced in the following year by Hisinger and Berzelius (Gehlen's Journal). Davy, in 1807, by the aid of the galvanic battery, discovered Potassium and Sodium, and afterwards succeeded in establishing the metallic nature of Barium, Strontium, and Calcium. Lithium was discovered in 1818, by Arfwedson ; Cadmium in the same year by Stromever; Zirconium, in 1824, by Berzelius; Aluminum, Glucinum, and Yttrium, by Wöhler, in 1828. Thorium was discovered by Berzelius in 1829 (Pogg. Ann.); Magnesium by Bussy, in the same year : Vanadium by Seftström, in 1830 (Ann. Ch. et Ph. xlvi.); Lanthanum by Mosander, in 1838 (Pogg. Ann.) In 1841, Didymium was discovered by the same chemist (Pogg. Ann. 504); and in 1843 he announced two other new metals,-Erbium and Terbium (Ann. Pharm. xlviii. 219.) Ruthenium was discovered by Kalus in 1844; Pelopium and Niobium by H. Rose in 1845. Finally, Norium, a metal of which little is as yet known, was announced in 1849 by Svanberg (Pogg. Ann. lxv. 317).

#### PHYSICAL CHARACTERS OF THE METALS.

THE metals are a class of simple substances, possessed of a peculiar lustre, having the property of conducting heat and electricity with great facility; but both in their chemical and physical properties they differ very much from each other, and are consequently applicable to a great variety of uses.

Those at present known amount to fifty-one in number, and are enumerated in the following table, with their equivalent numbers and symbols annexed.

		Equiv	alents.
	Symbols.	Hydrogen 🛥 1	$\begin{array}{l} \text{Oxy.} = 100 \\ \text{H.} = 12.5 \end{array}$
1. Aluminum	Al	13.69	171.17
2. Antimony (Stibium) .	Sb	129.03	1612.90
3. Arsenic	As	75.00	937.50
4. Barium	Ba	68·64	858.01
5. Bismuth	Bi	70.95	886.92
6. Cadmium	Cd	55.74	696.77
7. Calcium	Ca	20.00	250.00
8. Cerium	Ce	<b>46</b> .00	575.00
9. Chromium	Cr	28.15	351.82
10. Cobalt	Co	29.52	368.99
11. Copper (Cuprum)	Cu	31.66	395.70
12. Didymium	Di		
13. Erbium	Er		
14. Glucinum	Gl	26.50	331.26
15. Gold (Aurum)	Au	98.33	1229.16
16. Ilmenium	II		
17. Iridium	Ir	98.68	1233.50
18. Iron (Ferrum)	Fe	28.00	350.00
19. Lanthanum	Ln	48.00	600.00
20. Lead (Plumbum)	Pb	103.56	1294.50
21. Lithium	Li	6.43	80.37
22. Magnesium	Mg	12.67	158.35
0	0	-	

TABLE OF METALS.

#### PHYSICAL CHARACTERS OF THE METALS.

		Equivalents.			
echenologi, olige på sinde ett e angeograpi, to entres affantes	Symbols.	Hydrogen= 1	0xy. = 100 H. = 12.5		
23. Manganese	Mn	27.67	345.90		
24. Mercury (Hydrargyrum)	Hg	100.07	1250.90		
25. Molybdenum	Mo	47.88	598.52		
26. Nickel	Ni	29.57	369.68		
27. Niobium	Nb	Shin anider	Tarih Sana Villa		
28. Norium	Nr	The The Same	Contraction of the second		
29. Osmium	Os	99.56	1244.49		
30. Palladium	Pd	53.27	665.90		
31. Pelopium	Pp	nation material 3	al and allow		
32. Platinum	Pî	98.68	1233.50		
33. Potassium (Kalium) .	K	39.00	487.50		
34. Rhodium	R	52.11	651.39		
35. Ruthenium	Ru	52.11	651.39		
36. Silicium	Si	21.35	266.82		
37. Silver (Argentum)	Ag	108.00	1350.00		
38. Sodium (Natronium) .	Na	22.97	287.17		
39. Strontium	Sr	43.84	548.02		
40. Tantalum or Columbium		92.30	1153.72		
41. Tellurium	Te	66.14	801.76		
42. Terbium	Tr		and a state		
43. Thorium	Th	59.59	744.90		
44. Tin (Stannum)	Sn	58.82	735.24		
45. Titanium	Ti	24.29	303.66		
46. Tungsten (Wolfram) .	W	94.64	1183.00		
47. Uranium	U	60.00	750.00		
48. Vanadium	V	68.55	856.89		
49. Yttrium	Y	32.20	402.51		
50. Zinc	Zn	32.52	406.59		
51. Zirconium	Zr	33.62	420.20		

These may be divided into two classes or divisions. The first class consists of those which have so great an affinity for oxygen that they combine with it at the ordinary temperature of the atmosphere, and become rapidly oxidised, even when protected from the influence of moisture, and are consequently never used in the arts in an uncombined state. Such are—

Potassium	Calcium	Erbium	Thorium
Sodium	Magnesium	Terbium	Cerium
Lithium	Silicium	Glucinum	Lanthanum
Barium	Aluminum	Zirconium	Didymium
Strontium	Yttrium	Norium	fanctins dearen 3D

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Those of the above metals which have been applied to useful purposes are either employed in combination with other simple substances, or united with acids in the form of salts, and in this state furnish the arts with a most valuable series of compounds. Thus, those in the first part of the series, when associated with oxygen, severally yield potash, soda, baryta, strontia, lime, magnesia, and alumina, which, either in their uncombined state, or united with acids, forming salts, are of hourly application to our wants. The other metals of this class have not hitherto been usefully applied, which arises from the circumstance that some of them do not occur in sufficient abundance to admit of their advantageous treatment, whilst the preparation of others is attended with great expense, and they are therefore replaced by bodies which allow of being manufactured at a cheaper rate.

The second class consists of those metals which have so slight an affinity for oxygen as to be but little affected by it at ordinary temperatures. These are—

Gold	Antimony	Iridium
Silver	Arsenic	Ruthenium
Copper	Cobalt	Osmium
Iron	Nickel	Titanium
Manganese	Chromium	Columbium
Mercury	Tungsten	Niobium
Tin	Molybdenum	Ilmenium
Lead	Vanadium	Pelopium
Zinc	Platinum	Uranium
Cadmium	Palladium	
Bismuth	Rhodium	

The metals belonging to this class are extremely numerous, but in order to render them extensively applicable in an uncombined state it is necessary they should fulfil certain physical conditions, without which they will be of little value.

In the first place, they must possess a certain tenacity and malleability, without which it would be impossible to manufacture them into the various forms which they are constantly required to assume. It is also important that the ores from which they are obtained should be found in considerable quantities, and that the extraction of the metals should not be attended with any extraordinary difficulty or expense, otherwise they could only be employed for special purposes for which others were unfitted, and could therefore never come into general use.

The more brittle metals are seldom employed alone, but usually in combination with others possessing a higher degree of malleability and ductility, and thus alloys are frequently obtained which exhibit most remarkable and valuable properties, combining, to a certain extent, the characteristics of the several metals of which they are formed.

The metals sufficiently malleable to enable them to be employed in an uncombined state are the following :---

Gold	Mercury	Nickel
Silver	Tin	Zinc
Platinum	Manganese	Cadmium
Palladium	Iron	Copper
Iridium	Cobalt	Lead

Of these, however, many have not been employed in the arts; and this arises either from the scarcity of the ores from which they are obtained, or from their place being advantageously supplied by other metals which can be procured at a cheaper rate.

**Opacity and Lustre.**—It has been before mentioned that the metals possess a great degree of opacity, and are remarkable for a peculiar lustre, called metallic. All, however, are not equally opaque, as gold, when reduced to extremely thin leaves, transmits rays of green light. Silver leaf of one-hundred-thousandth of an inch in thickness is perfectly opaque; but very thin leaves of an alloy of silver and gold appear of a blue colour when viewed by transmitted light.

The lustre of metals is a consequence of their opacity, and depends on their great power of reflecting light. When reduced to the state of powder, their peculiar metallic appearance disappears, but is immediately reproduced by rubbing with a burnisher, or any other hard and smooth substance.

**Colour.**—Most of the metals, when in a finely-divided state, are of a gray colour, but, when consolidated and polished, approach more nearly to white. The colours of some of them are, however, very decided : thus copper and tellurium are red, gold is yellow, and lead is blue.

The alloys formed by the mixture of different metals usually possess to a certain extent the colours of the metals of which they are composed. Those resulting from the combination of two or more gray or white metals will themselves be gray or white; but, if a coloured metal enter into its composition, the alloy will assume its colour in a marked degree, although, if the proportion of the coloured metal be small compared with the amount of that which is not coloured, this is not always very apparent.

Hardness.—The metals differ from each other in no respect more than with regard to their hardness. Those which are pure are usually less hard than their alloys, and many of them are so soft as to admit of being easily scratched with the nail, or even moulded between the fingers.

Titanium	
Manganese	Harder than Steel
Platinum	Ĵ
Palladium	e
Copper	¥
Gold	
Silver	Scratched by Calc Spar
Tellurium	
Bismuth	
Cadmium	
Tin	J
Chromium	Scratch Glass
$\mathbf{R}$ hodium	f Scratch Glass
Nickel	)
Cobalt	
Iron	Scratched by Glass
Antimony	
Zinc	j –
Lead	Scratched by the nail
Potassium	Soft as wax at 60° Fah.
Sodium	)
Mercury	Liquid at ordinary temperatures.

The following table, arranged by Dumas, shows the relative degrees of hardness of some of the more common metals :---

**Density.**—The specific gravity of the different metals differs extremely, as among them we find some bodies possessing a density at least twenty times greater than that of water; whilst others weigh less than half their bulk of that liquid.

The principal metals, arranged according to their specific gravity, are given in the following table. Water = 1.000; temp.  $= 60^{\circ}$  F. (Brande's Manual of Chemistry.)

Platinum			20.980	Nickel .			8.27
Gold .			19.258	Iron			
Iridium			18.680	Molybdenur	n		7.40
Tungsten	÷.		17.500	Tin <sup>°</sup>			
Mercury			13.568	Zine			
Palladium			11.800	Manganese			6.85
Lead .			11.350	Antimony			
Silver .			10.470	Tellurium			6.10
Bismuth			9.80	Arsenic .			5.88
Uranium	10		9.00	Titanium			5.30
Copper .			8.89	Sodium .			0.97
Cadmium				Potassium			0.86
Cobalt .			8.53				

8

**Crystallisation.**—All the metals are capable of assuming, under favourable circumstances, the crystalline form. Many of them particularly gold, silver, copper, and bismuth—occur crystallised in nature, and are found either as cubes or octahedrons, or in some of the derivative forms : antimony is, however, an exception to this rule, and affords rhomboidal crystals.

In order to crystallise a metal artificially, it is sometimes sufficient to melt a few ounces in a crucible, and, having permitted it to cool on the surface, to pierce the crust formed and allow the interior to flow out. By this means very beautiful crystals of bismuth may be obtained; but in the case of some of the less fusible metals larger masses and slower cooling are necessary to produce this effect, and consequently these are never found in a crystalline state unless considerable weights have been fused, and allowed gradually to cool, as sometimes occurs in the furnaces in which their metallurgic treatment is effected.

It also frequently happens that one metal may be precipitated in a crystalline form by placing a strip of another metal in the solution of its salts. In this way silver is deposited by mercury, and a piece of zinc placed in a solution of acetate of lead precipitates the latter in feathery crystals. Gold is occasionally deposited in this form from its ethereal solutions, and a stick of phosphorus produces the same effect. Nearly all the metals yield crystals when deposited from their solutions by electric currents of feeble intensity, and it is doubtless to this action that we are indebted for the many beautiful specimens of the native metals which enrich the cabinets of mineralogists.

**Malleability.**—When a piece of metal is struck by a hammer, it either flattens under the blow or splits with more or less facility into fragments : to the former property the name of malleability is applied, whilst metals possessing the latter peculiarity are termed brittle. The malleable metals may be reduced into thin leaves either by the hammer or by the flatting-mill.

This instrument consists of two metallic cylinders (A, B, fig. 1) placed horizontally one above the other. These, by means of cogwheels, are made to revolve in contrary directions,

as shown by the arrows. These rollers are so arranged in a frame as to admit of being placed, through the medium of strong screws, at any required distance from each other, or, if necessary, of being brought into actual contact. To reduce a piece of metal by this means into the form of a thin sheet, it should be first cast in the shape of a



rectangular ingot, having nearly the same width as the required plate. One of its ends is then flattened into the shape of a

wedge so as to enter easily between the rollers, which, on being set in motion, draw the metal in and pass it through on the other side reduced in thickness and much elongated. By repeating this operation several times, and gradually reducing the distance between the two cylinders, sheets of almost any degree of thinness may be obtained.

During this artificial compression of the metals, their molecular structure rapidly undergoes a change, and those which at first are soft and pass readily through the mill, soon become brittle and difficult to work. It is then said to be "rash," and requires to be softened by being heated to redness, and afterwards allowed to cool down very gradually to the temperature at which it is worked. This process is called annealing.

Gold is the most malleable of the metals, and is frequently made into leaves of only  $\overline{a}_{00000}$  th of an inch in thickness, each grain of which is found to cover a surface of fifty-four square inches. The metals are arranged in the following list according to the order of their malleability :---

1.	Gold	6. Platinum	11. Palladium
2.	Silver	7. Lead	12. Potassium
3.	Copper	8. Zine	13. Sodium
	Tin	9. Iron	14. Frozen Mercury
5.	Cadmium	10. Nickel	,

Ductility.—The above metals are also ductile, or capable of being drawn into wire, but do not possess this property in the same order as their malleability. Wire is manufactured by passing an oblong piece of metal through the progressively diminishing holes of a steel tool, called a draw-plate. By this means wires of almost any length or diameter may be obtained, as the metal takes the size of last hole through which it has passed. Silver, for the purposes of embroidery, is frequently made into wires  $\frac{1}{500}$ th of an inch in diameter. A grain of gold may be drawn into a wire 550 feet long by enveloping the ingot operated upon in a coating of silver, and then passing it through the draw-plate. The wire thus produced will also be found covered with silver, and on removing this latter metal by diluted nitric acid, an enclosed gold wire, of only  $\frac{1}{500}$  th of an inch in diameter, will be obtained. Platinum treated in the same way, may be made into wire not exceeding 300000 th of an inch in thickness (Phil. Trans. 1833, p. 114).

The following metals are arranged according to the order of their ductility :---

1. Gold

10

- 2. Silver
- 3. Platinum
- 4. Iron

- 5. Nickel 6. Copper
- 7. Zine
- 8. Tin

- 9. Lead
- 10. Palladium
- 11. Cadmium

Tenneity.—The power possessed by different metals of sustaining weights is very variable, and influences in a great degree their economic values. It is therefore important to ascertain by careful experiment their relative tenacities, and the various influences which may affect them in this respect. For this purpose wires of equal lengths and diameters are employed. These are firmly suspended by one end from a fixed point, A, fig. 2, and to the other extremity weights are successively and carefully added until its rupture is effected. The weight which causes the wire to break necessarily represents the tenacity of the metal of which it is composed, when compared with others in every respect similarly treated.

According to the experiments of Guyton Morveau, the following are the weights sustained by wires 0.787of a line in diameter (An. Ch. et Ph. xl. 78).

Iron wire	suppor	ts		 549.250	lbs.
		,,	•	 302.278	"
Platinum	,, ,	,	• •	274.320	"
Silver	,, ,	,		 187.137	,,
Gold	<b>3</b> 2 <b>3</b>	,		150.753	"
Zinc	,, ,	,	 	 109.540	>>
Tin	»» »	,		34.630	22
Lead	22 2	17		 27.621	22

**Fusibility.**—All the metals admit of being liquefied by the application of heat; but the temperatures at which they melt are extremely various. Mercury retains its liquid form during the most intense colds of our climate. Potassium and sodium fuse below the boiling point of water. Tin melts at about 440° Fah.; lead at 612°; and antimony at about 850°. Gold, silver, and copper require a cherry-red heat; iron, nickel, and cobalt fuse at a white heat; manganese and palladium are melted only by the strongest heat of a wind furnace; chromium, uranium, molybdenum, and tungsten, agglutinate but slightly when treated in the same way; platinum, iridium, rhodium, osmium, cerium, titanium, and columbium, yield only to a powerful voltaic current, or the flame of the oxyhydrogen blowpipe. The metals are arranged in the order of their fusibility in the following table (Turner, *Elem. Chem.*) :---

	Mercury       . </td							
	Tin $\ldots$ $442^{\circ}$ Crichton							
Fusible	Cadmium 450° Stromever							
below a -	Bismuth 4079)							
red heat	Lead. $\ldots$ $\ldots$ $612^{\circ}$ Crichton							
	Tellurium rather less fusible than lead. Klaproth							
	Arsenic undetermined							
	Zinc							
	Antimony little below redness							
	(Silver							
	$ \begin{array}{ccccc} \text{Copper} & . & . & . & . & . & . & . & 1994^{\circ} \\ \text{Gold} & . & . & . & . & . & . & . & . & . & $							
	Gold 2016°							
	Cobalt rather less fusible than iron							
	Iron, cast Daniell							
	Iron, malleable. require the highest heat of a smith's							
	Manganese forge							
	Nickel nearly the same as Cobalt							
Infusible	Palladium							
below a -	Molybdenum							
red heat	Uranium							
rea neat	Tungsten Almost infusible, and not							
	Chromium to be procured in a but-							
	Titanium ton by the heat of a							
	Cerium smith's forge, but fus-							
	Osmium ible before the oxy-							
	Iridium hydrogen blowpipe.							
	Rhodium							
	Platinum							
	Columbium							

Elasticity and Sonorousness are attributes of the harder metals only, and are more conspicuous in some of their alloys than in the metals themselves.

**Odour and Taste.**—Many of the metals, when rubbed or otherwise slightly elevated in temperature, possess a singular and characteristic odour, and if applied to the tongue leave a peculiarmetallic taste. This property has been attributed to the voltaic action caused by the saliva between the metals and their impurities : since, however, similar phenomena present themselves when per-

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fectly pure specimens are selected, it is not probable that this explanation is correct.

**Power of Conducting Heat.**—Some of the metals transmit heat with much greater facility than others, and are consequently well adapted for the manufacture of boilers and other apparatus employed for the generation of steam, as also for stove-pipes, and all purposes where it is of importance that the heat acquired by the metallic surfaces should be readily communicated to surrounding bodies.

In the following table the metals are arranged in the order of their decreasing conducting powers, and opposite to the name of each body is placed the approximative ratio of the facility with which it transmits heat (Regnault's *Cours Elémentaire de Chimie*).

Gold .		200	Iron		75	Tin .		64
Silver		195	Zinc		73	Lead		36
Copper	•	180				CELL BERRY		

**specific Heat.**—The amount of heat required to raise equal weights of the different metals to the same temperature is very variable. Thus, if we express by 1.000 the quantity of caloric necessary to raise a pound of water from 32° Fah. to 212°, that which must be supplied in order to elevate the same weight of the following metals to that temperature, will be as below :—

Gold				0.0324 Regnault
Silver				0.0570 "
				0.0324 "
TD 11 1'				0.0593 "
Iridium .				0.0368 ,,
Mercury .				0.0318 De la Rive and Marcet
Copper .				0.0950 ,, ,,
Nickel .	. 2			0.0950 " " 0.1086 Regnault
Cobalt .				0.1172 De la Rive and Marcet
Iron				0.1130 Potter
Lead				
Tin				0.0560 "
Zinc				0.0929 Newman
Cadmium .				0.0567 Regnault
Antimony .				0.0508 ,,
Bismuth .				0.0270 Newman
Arsenic				0.0814 Regnault
Manganese .				0.1441 "
Uranium .	1			0.0619 "
Molybdenum				0.0659 De la Rive and Marcet
				0.0364 Regnault

**Expansion.**—Heat has the property of removing the integral' particles which constitute a body to a greater distance from each other. The substance becomes less compact, and therefore occupies more space than it did previous to the application of heat,— or, in other words, it expands.

The linear expansion of the metals, on being heated from 32° Fah. to 212°, is given in the following table :—

Gold $0.00155155 = \frac{1}{561}$ st Lavoisier & Laplace
Silver $0.00190868 = \frac{661}{1224}$ th "
Platinum $0.00099180 = \frac{524}{1008}$ th Houghton
Palladium $0.00100000 = \frac{1008}{1000}$ th Wollaston
Copper $0.00171733 = \frac{1}{582}$ nd Lavoisier & Laplace
Iron $0.00123504 = \frac{1}{812} \text{th}$
Lead $0.00284836 = \frac{11}{551}$ st "
Tin (from Malacca) $0.00193765 = \frac{1}{516}$ th "
Zinc (cast) $0.00294167 = \frac{310}{540}$ th Smeaton
$Z_{inc}$ (hammered) 0:00310833 — 1 nd
Bismuth $0.00139167 = \frac{1}{3^{1}5}$ th "
Antimony $0.00108333 = \frac{1}{92} \text{ ard}$ "

**volatility.**—All the metals are probably more or less volatile, although a certain number only admit of being readily converted into vapour at the highest temperatures of our furnaces : such are —zinc, cadmium, mercury, arsenic, antimony, tellurium, potassium, and sodium. Several others have the property of communicating characteristic colours to flame, and are therefore evidently volatile to a small extent.

# CHEMICAL PROPERTIES OF METALS.

THE success of every metallurgical process must depend on the chemical affinities of the minerals treated, and it is therefore of the utmost importance that the metallurgist should be well acquainted with the deportment of the various metals, both when combined with each other, and also when associated with the nonmetallic elements.

### THE METALS AND OXYGEN.

All the metals may be made to combine with oxygen, although their affinities for this body are extremely different. Some of them combine with it at all temperatures, and can only be reduced to the metallic state with great difficulty; whilst others possess so little affinity for this metal that they cannot be made to combine directly with it, and a slight elevation of temperature is sufficient to effect a separation.

The relative affinities possessed by the different metals for oxygen may be estimated in various ways.

1stly. By their deportment with oxygen gas, or common air, at ordinary temperatures.

2ndly. By the greater or less facility with which their oxides may be reduced to the metallic state.

3rdly. By their power of decomposing water under varying circumstances.

4thly. By their power of decomposing water acidulated with one of the stronger acids. In this way many metals, such as iron and zinc, effect at ordinary temperatures the decomposition of water acidulated with sulphuric acid, giving rise to the evolution of hydrogen gas. Others, on the contrary, do not produce this effect, even when strongly heated.

The decomposition of acidulated water by a metal does not depend entirely on its power of combining with oxygen, but is influenced in a certain degree by the affinity of the oxide produced for the acid present, as also by the solubility or insolubility of the salt thus formed.

From the above considerations Regnault divides the metals into six groups : and as this method has the advantage of showing at a glance some of the most striking characteristics, and at the same time serves the purpose of an artificial memory, I shall adopt his classification in the present treatise.

First Group.—Metals which have the property of absorbing oxygen at all temperatures, even the most elevated, and of decomposing water even at the lowest, producing at the same time abundant evolution of oxygen gas. These are—

Potassium	Lithium	Strontium
Sodium	Barium	Calcium

The three former are called alkaline metals; the three latter are the metallic radicals of the alkaline earths.

second Group.—These metals consist of such as absorb oxygen at the most elevated temperatures, and of which the oxides are not reduced by the application of heat alone: these metals do not sensibly decompose water at low temperatures, but do so very decidedly when heated above 122° Fah. They are—

Manganese	Magnesium	Aluminum

To these we may also probably add the following, the decomposing power of which on water has not as yet been sufficiently studied :---

Glucinum	Thorium	Didymium
Zirconium	Cerium	Erbium
Yttrium	Lanthanum	Terbium

Third Group.—Metals which decompose water at a red heat, of which the oxides are not reducible by heat alone, and which do not decompose water at temperatures inferior to 212° Fah. All these decompose water in the cold when acidulated by the stronger acids. They are—

Iron	Chromium	Cadmium
Nickel	Vanadium	Uranium
Cobalt	Zinc	

The temperature at which these decompose water and absorb oxygen depends in a great measure on the state of division in which they exist, when exposed to oxidising influences. Iron, even when reduced to the state of filings, does not absorb oxygen with rapidity at ordinary temperatures. If, however, it be heated to dull redness in pure oxygen, the action is so rapid as to produce the phenomena of heat and light. If the metal be obtained in a still higher state of division, as by the reduction of its oxide by hydrogen gas, its mere exposure to cold atmospheric air will produce the same effects.

A bar of iron will not decompose steam at ordinary temperatures, but iron filings readily do so below 450° Fah. Fourth Group.—Metals which absorb oxygen at a red heat, and consequently cannot be reduced to the metallic state by heat alone. These decompose steam with great facility, but do not effect the decomposition of water in presence of the stronger acids. This latter phenomenon arises from the circumstance that the oxides of these metals afford but feeble bases, whilst most of them in the presence of the stronger bases, such as potash and soda, act the part of acids. From this cause most of the metals in the following list decompose water in the presence of the alkalies with evolution of hydrogen gas.

Tungsten	Tantalum	Tin
Molybdenum	Titanium	Antimony
Osmium		and succession of the

To these we may probably add-

Niobium

Ilmenium

# Pelopium

Fifth Group.—Metals which absorb oxygen at a red heat, and of which the oxides are not reduced by heat alone: they decompose water at extremely elevated temperatures only, and even then but very feebly. These metals do not decompose water either in the presence of acids or alkalies. They are—

Copper	Lead		Bismut	h	
Sixth Group.—Metals metallic state by heat al		are	reduced	to	the

Mercury	Iridium	Ruthenium
Silver	Palladium	Gold
Rhodium	Platinum .	

It may be here remarked, that all the metals of which the oxides are not decomposed by heat alone, are capable of decomposing water at more or less elevated temperatures. This arises from the circumstance that water, when very strongly heated, resolves itself into its elements; and when this is done through the medium of an oxidisable metal, it unites with the oxygen to form an oxide, whilst the hydrogen escapes in the gaseous form. If, instead of such a metal, a platinum wire, ignited by the voltaic pile, be used, small bubbles of gas will be seen to escape, and these on examination are found to consist of oxygen and hydrogen in equivalent proportions.

Of the Conditions which determine the Oxidation of the Metals. When a metal unites with oxygen, the combination is usually attended with heat; if the action be very rapid, combustion, together with intense light, is frequently the result. The combus-

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tion of the metals in oxygen gas goes on most rapidly when they are reduced to the state of powder previous to being subjected to its action, as in many instances the coating of oxide at first formed quickly prevents further change. For this reason, a stout copper wire, if heated to redness, and immersed in a jar of oxygen, rapidly becomes covered with a coating of oxide, which quickly protects the metal from further action; but if copper filings be treated in the same way they instantly ignite, and are converted into oxide of copper. If the oxide produced by the ignition of a metal in the gas is fusible at the temperature obtained by its combustion, it will be unnecessary to reduce it to powder, as the continual melting of the oxide constantly exposes a clean metallic surface to the further action of oxygen. For this reason, iron and steel, previously heated to redness, and immersed in a jar of oxygen, burn with great violence, even when exposed in large masses.

The volatile metals, when similarly treated, burn with great rapidity, as the first application of heat gives rise to the production of vapours which are quickly consumed and as rapidly replaced by another portion generated by the heat produced from the combustion of the first. Many of the metals may be kept indefinitely exposed at ordinary temperatures, to the action of perfectly dry oxygen without combination ; but if moisture be admitted, chemical action is at once set up, and the metal rapidly oxidised. The polish of a bar of iron is not impaired by being kept in a jar of dry oxygen, but a moist atmosphere soon produces a deposit of oxide which rapidly increases, and finally destroys it. In the case of some of the metals, such as zinc, the coating formed is very superficial, and serves to protect its surface from further action. The oxidation of many of the other metals, on the contrary, goes on after a certain time has elapsed with greater rapidity than at the commencement of the action. This arises from the coating of oxide formed being in an electro-negative state with regard to the unoxidised metal, and a voltaic pair is thus established, which continues in action as long as there is any portion of unoxidised metal remaining.

The presence of acid vapours in the air very much accelerates the oxidation of the metals. When a piece of iron is acted on by a humid atmosphere, it is attacked by oxygen dissolved in the watery vapour, and as the oxide of iron formed possesses a certain basic affinity for water, the action is thereby increased. In this way iron, and zinc, which do not decompose water at ordinary temperatures, and may be indefinitely preserved in that fluid when deprived of its dissolved oxygen by boiling, are, by the addition of a few drops of sulphuric, or any other strong acid, rapidly attacked. The affinity of the metal for oxygen is thus increased, and the oxide formed at once combines with the acid present, giving rise to a soluble salt, which being dissolved in the water, constantly leaves a clean metallic surface to be in its turn converted into oxide.

The metals of which the oxides possess acid properties, such as bismuth, tungsten, and antimony, oxidise with more rapidity when moistened with alkaline solutions before being exposed to the air, than if acted on by watery vapour alone.

Classification of the Metallic Oxides.-The oxides of the various metals vary extremely in their properties. Some of them act the part of strong bases, and in combination with acids form welldefined and permanent salts: others, on the contrary, possess acid properties, and themselves combine with other metallic oxides to form salts of more or less stability; whilst a third class exhibit such feeble affinities that they sometimes act as bases, and at others as acids. Alumina may be given as an example of this description of oxides. Another class consists of what may be called exceptional oxides. These neither unite with acids or alkalies, but in presence of the stronger acids abandon a portion either of their oxygen or their metal, and form salts. The peroxide of manganese Mn O2 is of this class, and when heated with strong sulphuric acid gives up half its oxygen in the gaseous state, and forms the sulphate of the protoxide of manganese, MnO, SO<sub>3</sub>. The suboxide of lead, Pb<sub>2</sub>O, on the contrary, gives up half its metal when acted on by an acid, and gives rise to salts of the protoxide of the form PbO, M, in which M represents an acid. A similar decomposition is frequently effected in these oxides by heating them with some of the stronger fixed bases. In this way the oxide of manganese Mn O2, is converted into the sesquioxide Mn, Os, and manganic acid Mn O<sub>3</sub>, which combines with the base present. Thus, if potash be the base employed, the reaction is expressed by the following equation :---

# $3 (Mn O_2) + KO = Mn_2 O_3 + KO, Mn O_3$

The basic metallic oxides are also frequently found to combine with the higher oxides of the same metal possessing acid properties, and thus form a series of salts in which different oxides of the same metal act the part of acid and alkali. The oxides of iron Fe<sub>3</sub> O<sub>4</sub>, of manganese Mn<sub>3</sub> O<sub>4</sub>, and of chronium Cr<sub>3</sub> O<sub>4</sub>, are examples of these compound or saline oxides, and should be expressed by the formulæ—FeO, Fe<sub>2</sub>O<sub>3</sub>; MnO, Mn<sub>2</sub>O<sub>3</sub>, and Cr O, Cr<sub>2</sub>O<sub>3</sub>. The brown oxide of chromium Cr O<sub>2</sub>, and antimonious acid Sb O<sub>2</sub> are both compounds of this class, and should be expressed by the formulæ— $Cr_2 O_3$ ,  $Cr O_3 = 3$  ( $Cr O_2$ ) and  $Sb_2 O_3$ ,  $Sb_2 O_5 = 4$  ( $Sb O_2$ ).<sup>1</sup>

Some of the metals form a great variety of compounds with oxygen; and manganese in particular furnishes remarkable examples of each of the oxides above described. Mn O the protoxide of manganese is a powerful base.  $Mn_2 O_3$ , is an indifferent oxide, sometimes behaving as a base, and sometimes as an acid.

The peroxide Mn  $O_2$  is an example of an exceptional oxide, and is decomposed by an acid into the protoxide, which combines with it to form a salt, and into oxygen gas which escapes.

The oxide  $Mn_3 O_4$  is a compound oxide or manganite of oxide of manganese, and should be written MnO,  $Mn_2 O_3$ .

Lastly, manganic acid Mn  $O_3$ , and hypermanganic acid Mn  $O_5$ , combine with the bases, and form numerous and well-defined salts,

**Preparation of the Metallic Oxides.**—The metallic oxides are variously prepared. Many metals absorb oxygen on being heated in presence of common air or oxygen gas, in the same way some of the lower oxides are made to combine with a further portion of oxygen. The protoxide of manganese Mn O heated in contact with air is converted into sesqui-oxide  $Mn_2 O_3$ . The protoxide of barium (baryta), heated to a temperature of about 700° Fah. in an atmosphere of oxygen, absorbs another equivalent of the gas; but if the temperature be elevated much above this point, protoxide of barium is again formed.

By exposure to heat many of the higher oxides lose a portion of their oxygen. The peroxide of lead Pb  $O_2$ , and the sesquioxides of nickel and cobalt Ni<sub>2</sub>  $O_3$  and Co<sub>2</sub>  $O_3$ , are by this means converted into the protoxide Pb O, Ni O, and Co O. On this fact also depends one of the most common methods of making oxygen; as, when the peroxide of manganese Mn  $O_2$  is heated to redness, it gives off a part of its combined gas, and leaves the sesquioxide of manganese Mn<sub>2</sub>  $O_3$  in the retort.

The oxides of some of the metals, and particularly those which possess acid properties, are requently to be obtained by heating the metal with substances which easily yield their oxygen. If powdered antimony be thrown into a red-hot crucible containing fused nitrate of potash, this salt will be decomposed with the formation of antimoniate of potash, which, on being decomposed by an acid, deposits antimonic acid Sb<sub>2</sub> O<sub>5</sub>. In the same way, by fusing oxide of chromium with nitre, chromate of potash is obtained, from which the chromic acid Cr O<sub>3</sub> is readily separated by the addition of sulphuric acid.

Many of the higher oxides are obtained by heating either the <sup>1</sup> Some chemists double the equivalent of antimony, and make the protoxide Sb  $O_{3}$ .

metal or a lower oxide with nitric acid, and then evaporating to dryness. Some of the metals, such as tin and antimony, leave an insoluble peroxide in a free state when thus treated. Others, and these are by far the greater number, form nitrates, which, on being heated to redness, are decomposed, and a metallic peroxide is left.

All the carbonates, except those of the metals of the first group, are decomposed at high temperatures, giving rise to the evolution of gaseous carbonic acid, and the production of a free oxide. In this way, lime, barytes, and strontia are obtained, by calcining their respective carbonates; and the carbonate of lead, similarly treated, will be found to yield its carbonic acid with still greater facility.

When heated to redness in a current of hydrogen gas, many of the higher oxides are reduced to the metallic state; others are merely converted into protoxides, and resist all further efforts at reduction by this means.

The metallic oxides can frequently be prepared by precipitation from their salts, through the medium of an alkaline base, or ammonia. If we pour caustic potash into a solution of protosulphate of iron, a precipitate of hydrated protoxide of iron will be obtained. The following equation will explain the reaction :----

### $FeO, SO_3 + KO, HO = KO, SO_3 + Fe O, HO$

If the protochloride of iron were employed, the reaction would be as follows :---

## Fe Cl + KO, HO = KCl + FeO, HO

The same reagent produces in solutions of the sesquioxide the following changes :---

## Fe<sub>2</sub> O<sub>3</sub>, $3 \text{ SO}_3 + 3 \text{ KO}, \text{HO} = 3 (\text{KO}, \text{SO}_3) + \text{Fe}_2 \text{ O}_3 \text{ HO}$ Fe<sub>2</sub> Cl<sub>3</sub> + $3 \text{ KO}, \text{HO} = 3 (\text{K Cl}) + \text{Fe}_2 \text{ O}_3, \text{ HO}$

Here the protoxide of iron is replaced by the sesquioxide contained in the salt, which like the former is precipitated in a hydrated state. On heating the hydrated protoxide of iron, the water is expelled, and, from the absorption of oxygen, anhydrous sesquioxide of iron remains.

The peroxide of hydrogen is sometimes employed for the oxidation of those bases which resist less energetic means, and in this way the peroxide of calcium, and some other peroxides, are obtained.

Action of the non-metallic elements on the Oxides. Oxygen and the Oxides.—The lower metallic oxides usually combine with a further portion of oxygen when exposed to the air. In some instances this takes place at ordinary temperatures, and in a dry atmosphere, but the action is much accelerated either by the presence of water or the application of heat. The precipitated hydrates of the protoxides of iron and manganese are rapidly converted, by exposure to the air, into the hydrates of the sesquioxides of those metals. In other instances a certain heat is required to produce this effect. Thus the protoxide of lead, when heated to about 720° Fah., is converted into a higher oxide (minium), which is again decomposed into protoxide if the heat be raised much above that point.

Hydrogen and the Oxides.---The oxides of all the metals, except those of the two first groups, are reduced to the metallic state by the combined action of heat and hydrogen gas. Those of the sixth group are decomposed by it at temperatures little superior to the boiling point of water, although a red heat is required for the reduction of the other oxides. On passing a current of hydrogen gas over peroxide of iron heated to redness in a porcelain tube, decomposition takes place. Hydrogen combines with the oxygen of the oxide, forming water, which is driven off, and metallic iron remains in the tube. If, on the contrary, iron filings are placed in the heated tube, and the vapour of water passed over them, the decomposition gives rise to hydrogen gas and peroxide of iron. These experiments, if isolated, would lead to very different conclusions. From the first we should infer that oxygen has a greater affinity for hydrogen than for iron, whilst it would appear from the latter, that oxygen has a greater affinity for the metal than for the gas. This apparent anomaly is accounted for by supposing the decomposition to be influenced by the relative quantities of the bodies present. Thus, in the former instance, every atom of oxide being at a given time within the influence of a great number of atoms of hydrogen, it is decomposed by it; whilst in the latter case the metallic particles may be regarded as being present in greater quantity, as those of the hydrogen will be carried off as soon as generated, by the current of watery vapour, and cannot therefore act as a reducing agent on the metallic oxide. From these considerations it is evident that the relative proportions of metal and watery vapour should vary both with the temperature and rapidity of the current, and that a point must exist at which, from the equal balance of the two, no action can take place either on the metal or its oxides.

**Carbon and the Oxides.**—All the oxides which are decomposed by hydrogen are also reduced to the metallic state by carbon; and potassa and soda, which are not reduced by hydrogen, are, at very elevated temperatures, deprived of their oxygen by the action of carbon, carbonic acid and carbonic oxide gases being evolved.

Action of Sulphur on the Oxides.—When the oxides of metals of the first group are heated in contact with sulphur, decomposition ensues, and a mixture of sulphate and sulphide is produced. If carbon in any form be present, its affinity for oxygen determines the decomposition of the sulphates, and sulphides alone are formed.

The oxides of the metals of the second class are not affected by being heated with sulphur, but many of them may be transformed into sulphides, by being mixed with finely divided charcoal, and afterwards subjected, at a high temperature, to the action of sulphur vapour. The oxides of the metals of the four last groups are all converted into sulphides, with formation of sulphurous acid gas, by the action of sulphur at a high temperature. Some of them, however, require the addition of carbon, and are not affected unless the vapour of sulphur is passed over them when thus prepared.

Chlorine and the Metallic Oxides .- The changes produced by the reaction of chlorine on the metallic oxides vary with the circumstances under which they are brought into contact with each other. All the oxides, with the exception of a few belonging to the second group, are converted into chlorides by the action of dry chlorine gas. Considerable elevation of temperature is, however, sometimes necessary to effect this decomposition, and the action is usually much accelerated by the addition of a portion of powdered charcoal. The best method of converting the metallic oxides into chlorides is to mix them intimately with lamp-black and oil, and when the mass has assumed the proper consistence it is divided into small pellets of the size of peas. These are introduced into a large porcelain tube, heated to redness, through which chlorine is passed, and by this means the oxides of all the metals may be converted into chlorides. In this reaction the affinity of carbon for oxygen assists that of the chlorine for the metal, and the results are carbonic oxide and a metallic chloride.

If the oxides are held in solution or suspension in water, very different results are obtained; the products often vary according to the temperature and strength of the solution employed. When chlorine gas is passed into a weak solution of potash, the temperature of which is prevented from rising by means of a freezing mixture, or otherwise, a reaction is set up between two atoms of potash and two of chlorine, attended by the production of one equivalent of hypochlorite of potash, and one of chloride of potassium.

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Should a strong solution of potash be employed, and the temperature be allowed to rise, six equivalents of potash and six of chlorine will react on each other, yielding one atom of chlorate of potash, and five of chloride of potassium: thus 6 KO + 6 Cl = KO, Cl O<sub>5</sub> + 5 K Cl. The same occurs with the oxides of all the metals of the first group, but the production of the chlorates is found to be more rapid at moderate temperatures than when the solution is permitted to boil.

With the exception of the oxides of manganese and magnesium, the metals of the second class are not, when held in suspension or solution in water, decomposed by a current of chlorine gas.

Chlorine transforms the oxides of the metals of the third class, when held in suspension in water, at first, into protochlorides and peroxides; but if the action be long continued, a mixture of perchloride and peroxide will be the result. The sesquioxides of the metals of this class, suspended in water, are not acted on by chlorine, except in presence of an alkali. When the sesquioxide of iron, Fe<sub>2</sub> O<sub>3</sub>, suspended in a solution of potash, is thus treated, it takes up an additional quantity of oxygen at the expense of the potash, and chloride of potassium and ferrate of potash are formed. The following equation will explain this decomposition :—

## $Fe_2 O_3 + 5 KO + 3 Cl = 2 (KO, Fe O_3 + 3 KCl)$

The oxides of the metals of the three last groups, when suspended in water, resist the action of chlorine. The action of iodine and bromine on the metallic oxides very closely resembles that of chlorine on the same compounds.

Action of Chlorine on the Metals.-Chlorine unites with all the metals, at temperatures more or less elevated. Minute division very much accelerates this combination, and in many instances causes the action to be so rapid as to be attended by the ignition of the metal. Powdered copper, antimony, and arsenic burn when thrown into a jar of chlorine; mercury and iron inflame when slightly heated in it, whilst it is quietly absorbed by gold, silver, and platinum. The metallic chlorides differ extremely in their physical and chemical properties. They exist of almost every Some of them are decomposed by heat, whilst others are colour. not affected by it. Some are soluble in water, and others are totally insoluble. Some are permanent in the air, whilst others are deliquescent. Many of them decompose water, and give rise to an oxide and hydrochloric acid; others, on the contrary, are in no way affected by moisture.

The methods employed for the preparation of the various chlorides differ according to the state in which the metal exists, and has also reference to the properties of the chloride formed. All the metals may be made to combine with chlorine, by heating them in a current of that gas. This arises not only from the affinity possessed by chlorine for metallic bodies, but the action is also much aided by the fusibility of the resulting compounds, as the chlorides being all more or less fusible, constantly leave exposed a clean surface for the further action of the gas.

The soluble chlorides are generally prepared by dissolving the metal in hydrochloric acid, which is attended by the evolution of hydrogen gas. The protochlorides of the metals of the third group are easily prepared in this way. The metals of the fifth group do not, even at the boiling point, effect the decomposition of hydrochloric acid, but, if nitric acid be added, a chloride is at once formed. When the metals of the third group are thus treated, bichlorides are produced.

The insoluble chlorides are usually obtained by precipitation from a soluble salt of the metal. Thus chloride of silver is precipitated from the soluble nitrate of silver by the addition of hydrochloric acid, common salt, or of an aqueous solution of chlorine, and is therefore employed by the chemist as a delicate test for the presence of that body.

The metallic chlorides, with the exception of those of gold and platinum, and probably a few others belonging to the same group, are not decomposed by the application of heat alone, although some of them are very volatile, and may be distilled from one vessel into another, without undergoing any further change.

Action of Oxygen on the Metallic-Chlorides.—Oxygen produces no change, even at a red heat, on the chlorides of metals of the first group. Those of the second, third, fourth, and fifth groups, are, on the contrary, changed into oxides, when heated to redness in a current of oxygen. The chlorides of the metals of the sixth group, which are decomposed by heat alone, are also decomposed when heated in a current of oxygen, but do not absorb any of that gas. Those, on the contrary, which are not affected by heat alone, remain unchanged in a current of oxygen gas.

Action of Hydrogen on the Metallic Chlorides.—The chlorides of the metals of the two first groups are not decomposed at any temperature by hydrogen gas. All those of the four last groups are decomposed by hydrogen at a red heat, with evolution of hydrochloric acid. Carbon produces no visible effect on the metallic chlorides.

#### SULPHUR AND THE METALS.

Sulphur combines with all the metals; and the resulting sulphides, except a few among those of the sixth group, are not affected by the application of heat alone. The sulphides or sulphurets are prepared in many ways :--

Istly, By heating the metal in a finely divided state in a close vessel containing sulphur, or by passing the vapour of sulphur over the metals, heated to redness in a porcelain tube. The action produced by this means is frequently so rapid that ignition of the metal ensues; and when copper, bismuth, lead, or iron filings are so acted on, the combination is attended with vivid combustion. If sodium or potassium be substituted for the metals above enumerated, their conversion into sulphides takes place with equal violence.

2ndly, By heating a mixture of the metallic oxides and sulphur, in which case sulphurous acid is evolved, and the sulphide formed remains in the crucible.

3dly, By calcining a mixture of the metallic oxides with sulphur and alkaline carbonates in a crucible lined with charcoal. In this operation the carbonate of potash or soda employed is first converted into a polysulphide, which, at an elevated temperature, is decomposed, and the sulphur thus set free combines with the metal reduced by the carbon present. When the oxides of the metals of the fourth group are thus treated, electro-negative sulphides are formed, and these combining with those of the alkalies present, constitute a sulphur salt.

4thly, By decomposing the metallic sulphates, either by heating them with a mixture of charcoal, or by passing a current of hydrogen gas over them when heated to redness in a porcelain or hard glass tube.

5thly, By the action of sulphuretted hydrogen in solutions of the metallic salts. This affords an easy method of obtaining the sulphides of the metals of the third group.

6 6thly, By the action of sulphide of ammonium, or some other alkaline sulphide, on the soluble metallic salts. This method is applicable to the salts of the metals of the third group which are not decomposed by the action of sulphuretted oxygen only.

When sulphate of the protoxide of iron is thus treated with sulphide of potassium, the following reaction takes place :---

$$FeO, SO_3 + KS = KO, SO_3 + FeS.$$

When salts of the metals of the fifth group are acted on by a solution of sulphide of ammonium, the first effect produced will be to throw down the sulphides of those metals; but on subsequently adding a further quantity of the precipitant, the sulphides at first thrown down will be redissolved, and a soluble sulphursalt formed.

Action of the Non-metallic Elements on the Sulphides.—When the sulphides of the metals of the first group are exposed to the combined action of heat and oxygen, both the metal and the sulphur become oxidised, and combining with each other in their modified states are converted into metallic sulphates.

The sulphide of magnesium, which is a metal belonging to the second group, is similarly converted into sulphate of magnesia; but the sulphide of manganese, a member of the same section, is, on the contrary, decomposed by the action of this gas. In this case the products of the decomposition vary with the temperature at which it is effected. If the heat employed be considerable, the sulphur is entirely expelled in the state of sulphurous acid, and the metal remains in the state of oxide. When a lower temperature is employed, a certain quantity of sulphate is formed at the same time, and the product consists of a mixture of sulphate and oxide of the metal.

The sulphides of the third and fifth groups behave, when heated with oxygen, precisely like the sulphide of manganese. Those of the metals of the fifth group are entirely converted into oxides, whilst the sulphur escapes as sulphurous acid gas.

Lastly, the sulphides of the sixth group are reduced to the metallic state when heated in contact with oxygen, as the sulphur goes off in the form of sulphurous acid, and the uncombined metal remains. Most of the metallic sulphides become converted into sulphates when exposed for a long period to the combined action of air and moisture, and in this way many of the mineral ores are naturally though slowly converted into soluble salts.

### SELENIUM AND THE METALS.

Selenium acts on the metals with nearly the same phenomena as sulphur; the selenides are, however, of much less frequent occurrence in nature than the sulphides, and are consequently of very secondary importance to the metallurgist. They may be prepared either by passing a current of seleniuretted hydrogen through solutions of metallic salts, or by heating the metals directly with selenium.

### PHOSPHORUS AND THE METALS.

Many of the metallic phosphides are natural productions sometimes found in considerable abundance. They may be prepared artificially in three different ways :---

1stly, By heating a mixture of phosphorus and the metal, or by projecting phosphorus into a crucible, in which the metal is held in a state of fusion. 2ndly, By heating a mixture of phosphoric acid and charcoal with a metal or its oxide.

3rdly, By passing a current of phosphuretted hydrogen through a solution of the metallic salts. But few of the phosphides can, however, be obtained by the humid process, as, when phosphuretted hydrogen gas is passed through metallic solutions, either a peculiar compound is obtained, as is the case with the salts of the protoxide of mercury, or the metal is reduced to the metallic state, as when gold and silver salts are thus treated; or no change is produced by its action, as happens with by far the greater portion of the metallic salts. The phosphides have generally a metallic lustre and crystalline texture. Those of the metals of the first group are decomposed by water with evolution of spontaneously inflammable phosphuretted hydrogen, and the formation of their respective oxides.

Nitrogen, cyanogen, and boron, may also be made to combine with the metals, but their compounds are of but little importance to the metallurgist, and may consequently be passed over without remark.

### OF THE COMBINATIONS OF THE METALS WITH EACH OTHER.— ALLOYS.

The metals, with but few exceptions, are capable of combining with each other, and thereby forming a class of compounds possessing more or less the properties of their several constituents. Alloys are generally more fusible and harder than the metals which enter into their composition; and as these properties may be regulated according to the relative amount of the various metals employed, an infinite number of modifications may be thus obtained. Copper is very malleable and ductile, but is difficult to fuse, and for many purposes does not possess the requisite hardness. In many instances these defects may be obviated by the addition of one-third of its weight of zinc, which, without much impairing its malleability, renders it fusible, heightens its colour, and at the same time communicates to it a proper degree of hardness. In the manufacture of cannon, a mixture is required not only sufficiently hard to withstand the friction of the shot during its passage through it, but also capable of resisting the corrosive action of the products arising from the combustion of gunpowder. It should likewise possess considerable toughness, without which the gun would be liable to burst. In many cases, and particularly for battery use, cast iron is employed, but when guns are required to be moved from place to place, the brittleness of that metal becomes a serious objection, as, unless made very thick and heavy, they would not be capable of withstanding the explosive force to which they are subjected. If copper were employed, it would in the first place be extremely difficult to mould, as, from the high temperature required for the fusion of that metal, it is liable to chill and produce air-holes in the casting; and in the second, would soon wear out, if made, from the rebound of the shot in passing from the breech to the muzzle during its discharge.

By the addition of ten parts of tin to ninety parts of copper, an alloy is obtained which answers all these conditions, and is also used under the name of bronze, for the manufacture of statues, and for various other ornamental purposes.

For printers' type an alloy is required at the same time hard, fusible, and which does not materially contract in cooling. Lead, which is a fusible metal, is evidently unfitted for this purpose by its softness, whilst zinc and bismuth are too liable to break under the pressure to which the types are exposed in the process of printing. By combining, however, twenty parts of antimony and eighty of lead, an alloy is produced which fulfils all these conditions, and furnishes us at a cheap rate with a material admirably adapted for the purpose intended.

It has long been a disputed question whether the alloys are chemical combinations of metals in definite proportions or merely mechanical mixtures, without regard to their atomic relations. It is, however, probable that they are in all cases, combined according to the laws of chemical affinity. Berzelius has observed that the acidifiable metals have the greatest tendency to combine with those which produce salifiable bases, and that antimony, arsenic, and tellurium, form with the other metals, definite compounds analogous to their native sulphides and phosphides. Many of the alloys, both natural and artificial, are also found to be capable of assuming a crystalline form, and this property may frequently be employed for the purpose of separating the truly chemical alloy from the mechanical admixture caused by the excess of one of its constituents.

It has been before stated, that by alloying the metals, we obtain compounds possessed of very different ductility, malleability, hardness, and colour, from those belonging to the bodies which enter into their composition; thus gold and lead, and gold and tin, form brittle alloys, and a minute quantity of arsenic added to copper renders it white. It is also to be observed that an alloy composed of two metals has seldom a density corresponding to the mean which should be obtained by calculation from the relative amounts and specific gravities of its constituents.

The following table, from Thénard (Traité de Chime, Vol. i.

p. 394,) shows in what cases the specific gravities of the compounds are superior, and when inferior to the mean of the combined metals.

Gold and Zine , Tin , Bismuth , Antimony , CobaltGold and Silver , Iron , Lead , Just , Copper , Tin , East , Tin , Antimony , Antimony Copper and Zine , Tin , Antimony , Antimony Copper and Zine , Tin , Antimony , Antimony , Antimony , Antimony Lead and Bismuth , Antimony Platinum and Molybdenum Palladium and BismuthGold and Silver , Iron , Lead , Silver and Copper , Nickel , Antimony , Antimony , AntimonyGold and Silver , Iron , Lead , Copper and Lead , Antimony , Antimony , Antimony, Gold and Silver , Iron , Lead , Nickel , Antimony , Antimony	Alloys possessed of greater specific gravity than the mean of their components.	Alloys having a specific gravity in- ferior to the mean of their com- ponents.
	", Tin ", Bismuth ", Antimony ", Cobalt Silver and Zine ", Lead ", Tin ", Bismuth ", Antimony Copper and Zine ", Tin ", Palladium ", Bismuth ", Bismuth ", Antimony Lead and Bismuth ", Antimony	., Iron " Lead " Copper " Iridium " Nickel Silver and Copper Copper and Lead Iron and Bismuth " Antimony " Lead Tin and Lead " Palladium " Antimony Nickel and Arsenic

Alloys are generally more oxidisable than their constituents taken singly. This probably arises from the circumstance of one of the metals being electro-negative with respect to the others, by which means electric action is set up, and the more positive metal rapidly oxidised.

The action of acids on alloys varies according to the relative amount of their constituents. Silver alloyed with a large quantity of gold is protected from the action of nitric acid, by which, under ordinary circumstances, it is rapidly attacked. Sometimes, however, the reverse of this takes place, and metals which are totally insoluble in certain menstrua are made to dissolve in them by the addition of a metal on which they have the power of acting. In this way, platinum, although of itself insoluble in nitric acid, may be dissolved by it when sufficiently alloyed with silver. Alloys consisting of two metals, the one easily oxidisable, the other pos-

30

sessing a less affinity for that element, may be readily decomposed by the combined action of heat and air. In this case the former metal will be rapidly converted into an oxide, except perhaps the last portion, which may in some degree be protected from further action by the oxide already formed. The increased affinity for oxygen exhibited by the more oxidisable metal, in presence of another less affected by this agent, is doubtless an electric phenomenon, and the action is in many cases so rapid as to produce combustion. This occurs when an alloy of three parts of lead and one of tin is heated in contact with air.

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## THE METALLIC SALTS.

THE consideration of this class of bodies belongs rather to the science of chemistry than to that of metallurgy, and I shall therefore confine myself to such generalities as may enable the student to understand the nature of the various processes hereafter to be described, and must refer him for further information to the different treatises on elementary chemistry, in which he will find this subject more fully discussed.

The compounds hitherto described have been for the most part the result of the binary combination either of a metal and a nonmetallic element, or of two metals with each other. The salts, on the contrary, are usually formed by the chemical union of two binary compounds possessing opposite electric energies, and having in consequence a greater or less affinity for each other.

The binary electro-negative element is called an acid, and is most frequently composed of two non-metallic elements, as in the case of sulphuric acid SO<sub>3</sub>, nitric acid NO<sub>5</sub>, and chloric acid ClO<sub>5</sub>, &c. &c. Sometimes, however, one of the elements of an acid is a metal, as in the case of ferric acid FeO<sub>3</sub>, manganic acid MnO<sub>5</sub>, stannic acid SnO<sub>2</sub>, antimonic acid SbO<sub>5</sub>, and many others.

Some of the sulphur acids also contain a metal, and we therefore find such compounds as the sulphides of antimony and tin possessed of acid properties. The base or electro-positive element of a salt is always a metallic compound. The sulphides and oxides of many of the metals belong to this class.

The greater number of acids are compounds of oxygen and a metallic or non-metallic element, whilst the oxides of the metals afford the most numerous class of bases. Many of the sulphides also combine and form salts, in which the acid is an electronegative sulphide or sulphur acid, whilst the base is a sulphide possessing opposite electric energies.

The double chlorides resulting from the combination of the electro-positive chlorides of the metals with the electro-negative chlorides of other metallic or non-metallic elements, again form a class of salts of which we have many examples, and of which the number will probably be much increased with the advancement of the science of chemistry.

The oxy-salts, or those in which both the acid and base consist either of a metallic or non-metallic oxide, form by far the most numerous and important class, and have therefore received the greatest attention, and are the most fully understood by chemists; consequently the following generalities may be considered as referring particularly to them.

**Neutrality.**—Salts are divided into acid, alkaline, and neutral. The characteristics on which this distinction is founded are easily defined, in the case of those formed by the union of the energetic acids and bases; but they become less clear if the compound be the result of the combination of powerful bases with feeble acids, or of the stronger acids with the weaker bases. This difficulty becomes still greater when the resulting salt is insoluble in water.

The vegetable-blue colours, especially the tincture of litmus, are the tests ordinarily employed for the purpose of ascertaining the state of a salt with regard to its neutrality. This colour is itself formed by the union of a red vegetable acid with an alkaline base, and the resulting compound possesses the characteristic blue colour of tincture of litmus.

When a more powerful acid is added to this organic salt, it replaces its vegetable electro-negative element, which, becoming free, again assumes its original red colour, and consequently indicates the presence of a free or feebly combined acid in the solution into which it has been poured. A test for the presence of a free or feebly combined alkali is obtained by reddening tincture of litmus by an acid, as the original blue colour of the salt is again produced on neutralising by an alkali the acid first added to produce the red colour. In order that these reagents should be as sensitive as possible to the action of acids and alkalies, it is necessary to observe the greatest care to prevent any excess either of alkali in the blue solution, or of acid in the red one, as, if this were not attended to, the first portion of the acid or alkali in the solution to be examined, would, as the case might be, be appropriated by the free acid or alkali present, and thereby introduce a cause of error in the experiment. If we in successive portions pour sulphuric acid, which strongly reddens the blue colour of litmus, into a fluid containing potash, which blues the red solution of that substance, we shall find that the action of the alkali will gradually become less intense, and that finally we shall arrive at a point at which neither an acid nor alkaline reaction can be perceived. The resulting sulphate of potash is then said to be neutral, and if we evaporate the solution to dryness, and examine the residue, we find it to consist of sulphuric acid and potash, united in the proportion of 40 of the former to 47 of the latter, in which composition it will be found that the amount of oxygen contained in the acid is three times greater than that united with the potassium to constitute the base, and the salt will consequently be expressed by the formula KO, SO<sub>2</sub>.

If, instead of using potash, we were to employ soda or lithia for the purpose of saturating the sulphuric acid, we should obtain sulphates of those bases, in which the oxygen in the acid would be again found to be triple that contained in the base.

Baryta and strontia change the reddened tincture of litmus into blue with almost the same intensity as potash or soda; but if we add sulphuric acid to the solution of these bases in water, a dense white precipitate will immediately be formed, and continue to be deposited until the solution begins to evince a slight acid reaction.

If we now separate the liquor by filtration, and evaporate to dryness, we shall find that it retains nothing in solution, as the sulphate of baryta formed is insoluble in water, and is therefore wholly retained in the solid state on the filter. On testing this salt we fail to obtain either an acid or alkaline reaction, as from its insolubility it is incapable of affecting the vegetable colours. By analysing the precipitate, however, we find the same relation in this case between the amount of oxygen in the acid and base, as was observed with regard to the other salts, and from such considerations as these, chemists agree to consider those sulphates as neutral in which the amount of oxygen in the acid is three times greater than that contained in the base. If nitric instead of sulphuric acid be added to a solution of potash, the alkali will, as in the former case, become neutralised, whilst the nitrate of potash formed is found to have the formula KO, NO5, in which the amount of oxygen in the acid is five times greater than that contained in the base. On repeating this experiment on the various bases, it will invariably be found that the ratio of the oxygen contained in the acid to that combined with a metal to form a base is as one to five, and consequently all nitrates are considered neutral that maintain this proportion.

Many of the stronger acids are united to a portion of water which appears to be essential to their constitution, and in these cases the hydrated acids may be considered as salts of water, which are decomposed by the alkalies merely because the oxides of the metals are more highly electro-positive than the oxide of hydrogen, and are therefore capable of forming with the acid a more stable salt. The less powerful acids, such as carbonic and sulphurous acid, and many others, are incapable of thoroughly neutralising the stronger bases with regard to the coloured reagents, as,

in however great excess they may be added, the compound will still be found to retain an alkaline reaction. If, for instance, a current of carbonic acid be passed for a considerable time through a saturated solution of potassa, a crystallised salt will be deposited, which, on examination, is found so constituted that the amount of oxygen contained in the acid is four times greater than that which enters into the composition of the base. On dissolving the salt thus formed in water, and adding to the solution a portion of potash of the same weight as that originally operated on, a new crystalline salt is obtained, in which the amount of oxygen contained in the acid is only twice the weight of that united with the potassium of the base; and as both these salts produce alkaline reactions on the vegetable coloured reagents, it becomes a matter of difficulty to decide which of the two should be regarded as the neutral carbonate of potash. If, however, these experiments be extended to the other metallic oxides, it will be found that those of the first group are alone capable of affording two series of carbonates, whilst the five other sections only yield those in which the oxygen of the acid is double that of the base. For this reason most chemists describe the salts having the general formula MO, CO<sub>2</sub> as the neutral carbonates, although a few still consider MO, C<sub>2</sub>O<sub>4</sub> should be thus regarded, from the circumstance of its more nearly approaching neutrality with regard to the coloured reagents.

The definition of neutral salt becomes still more indefinite in the case of the combinations which take place between the bases and what are usually called polybasic acids. To illustrate this variety we may take the salts of common phosphoric acid as an example. If an excess of phosphoric acid be added to a solution of soda, and with proper precautions evaporated to dryness, we obtain a salt represented by the formula NaO, POs + 2 HO, in which the amount of oxygen contained in the acid is five times greater than that contained in the base. On dissolving this salt in water, and adding to its solution a quantity of soda equal to that which it already contains, a salt is produced expressed by the formula 2 NaO, POs + HO, in which the ratio of the oxygen in the base to that in the acid is as two to five; and on again dissolving this salt in water, and adding another equivalent of soda, the whole of the water is displaced, and the salt 3 NaO, PO<sub>5</sub> is obtained, where the oxygen in the acid compared with that in the base is as three to five. Of these salts the first possesses an acid reaction on tincture of litmus, whilst the two second colour the reddened solution of litmus blue, and therefore exhibit alkaline properties. The vegetable reagents are in this case incapable of deciding the question of neutrality, and chemists have consequently been induced to change the meaning of the word by which is now generally understood an equivalent of acid united with its usual number of equivalents of base. According to this definition each of the three phosphates above described may be considered as a neutral salt. The first will be a phosphate containing an equivalent of oxide of sodium, and two of oxide of hydrogen. In the second the addition of another equivalent of the stronger base has replaced the less electro-positive oxide of hydrogen : whilst in the third salt the feebler oxide of hydrogen has been entirely eliminated, and its place occupied by the alkaline base.

These and similar considerations have suggested the idea that many of the substances called acids are in reality salts, and that they do not combine with the oxides of the metals, as is usually supposed, but rather with the metals themselves; water being in every instance produced at the same time.

Sulphuric acid  $SO_3 + HO$ , is considered to be a compound of one equivalent of sulphur, combined with three of oxygen, and further united with an atom of water, to form the socalled hydrated sulphuric acid. Nitric acid,  $NO_{b} + HO$ , is in like manner regarded as composed of one atom of nitrogen, combined with five of oxygen, and one of water. It is, however, evident that sulphuric acid may either be expressed by the formula  $SO_3 + HO$ , or  $SO_4 + H$ , and that nitric acid is equally well represented by the equations  $NO_5 + HO$ , and  $NO_6 + H$ . If we consider the latter expressions as the true representations of the state of aggregation of atoms in the acids in question, the formation of a salt must be regarded as merely a result of the substitution of a metal in the place of the hydrogen contained in the acid. The latter view of the constitution of acids, and the formation of salts, has not only the advantage of explaining many phenomena hitherto not fully understood, but also of reducing the oxacids and hydracids to one class; and this theory is consequently rapidly gaining ground among chemists.

The most powerful alkaline bases are usually the metallic protoxides, and these combine with the acids to form salts, in which a constant ratio exists, in each family, between the oxygen in the acid and that in the base. When an acid combines with a base which is not the protoxide of a metal MO, but a higher oxide, such as the binoxide  $MO_2$ , then will that binoxide be disposed to unite with two equivalents of acid, and the same ratio be retained. If, instead of being combined with a binoxide, the acid be united to a sesquioxide, the same relation is observed to exist, and if sulphuric acid be chosen for its saturation, the resulting salt will have the general formula  $M_2 O_3 + 3 SO_3$ , the ratio of one to three being still preserved. When an oxybase is acted on by a hydracid, a reciprocal decomposition of the two bodies takes place. The hydrogen of the hydracid combines with the oxygen of the base to form water, whilst the electro-positive element of the base unites with the electro-negative element of the hydracid to form a binary compound, corresponding in its composition to the oxybase employed. Thus on adding hydrochloric acid to soda, water and chloride of sodium are formed.

## NaO + HCl = NaCl + HO

If, instead of soda we employ the sesquioxide of iron, water and sesquichloride of iron will be the result.

### $Fe_2O_3 + 3 HCl = Fe_2Cl_3 + 3 HO.$

The saturation of an alkali, with regard to the coloured vegetable reagents, may generally be effected as completely, by means of the hydracids, as if an oxacid were employed for that purpose, and the resulting compounds are found to possess, in every respect, the characteristic properties of salts. In the case of the hydrosalts, like that of the formerly called oxy-salts, the hydrogen of the acid may be supposed to be merely replaced by a metal, and it is at once evident that  $SO_4$ , H, and Cl, H, differ, merely, in-asmuch that in the one the first member is a compound body, while in the other it is, as far as we yet know, a simple element.

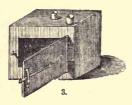
Nearly all salts are solid at ordinary temperatures. Those which are obtained by the combination of colourless acids with colourless bases are themselves colourless. The salts formed by the union of a coloured base with the various colourless acids are usually coloured, and when crystallised are all possessed of nearly the same tint as the bases which enter into their composition. Those formed by the union of the colourless bases with the coloured acids, are most frequently coloured, and exhibit for the most part the characteristic shades of the several acids in their free state.

Taste.—The taste of salts seems generally to depend rather on the nature of the base than of the combined acid. Thus, the salts of soda possess a flavour usually known by the name of saltness: those of potash are slightly bitter; whilst the compounds of magnesia are characterised by an insupportable bitterness. Sometimes, however, the flavour of a salt is considerably affected by the nature of the combined acid, as in the case of the sulphites, sulphur salts, and those formed by the combination of some of the metallic acids.

Water of Crystallisation.—A large proportion of the salts may be obtained either hydrated or anhydrous, according to the circumstances under which they are prepared. Many of the soluble salts are deposited from their solutions in combination with a certain quantity of water, which is called water of crystallisation. The quantity of water of crystallisation contained in a given salt, when crystallised at the same temperatures and from similar solutions, is always the same, and possesses a constant simple equivalent ratio with regard to the number of equivalents of acid and base entering into the composition of the salt. It therefore follows that the water of crystallisation contained in a salt is united according to the laws of definite proportion, and forms an essential chemical element of its composition, which, if abstracted, will be eliminated according to the same definite laws.

The hydrated salts abandon their water of crystallisation when strongly heated; and it is found that a constant amount of water is in the same salt retained for similar temperatures, although when that temperature is exceeded another portion of its water is eliminated, and a less highly hydrated salt is obtained. The sulphate of manganese affords a remarkable illustration of this fact. When that salt is allowed to crystallise from its solutions at a temperature below 43° Fah., its composition is expressed by the formula  $MnO, SO_s + 7 HO$ . If the crystals be obtained between the temperatures of 43° and 68°, the salt MnO,SO<sub>3</sub>+6HO, will be produced. On being allowed to crystallise between the lastnamed temperature and 86°, its composition will be expressed by the formula MnO,SO<sub>3</sub>+4HO. By crystallising at a temperature between 110° and 120°, a salt is obtained of which the composition is represented by MnO,SO<sub>3</sub>+HO: and finally, on heating the salt to 570°, the anhydrous sulphate of manganese MnO,SO<sub>2</sub> is obtained.

For the purpose of determining the quantities of water successively abandoned by a salt at different temperatures, an oilbath (fig. 3) is usually employed. This consists of two copper boxes, one of which is so placed within the other, that a space of



about an inch exists between them on all the sides except on that in which the door is placed. Before using the apparatus, this space is to be filled with oil by means of a tubulature, and a thermometer, of which the lower end is immersed in the oil, should be fitted to the other aperture by a perforated cork. This being done, the bath is

supported over a gas burner by an iron stand, and after having accurately weighed a certain quantity of the salt to be operated on, in a watch-glass or small capsule, it is heated to the required temperature, as indicated by the thermometer, until repeated weighings show it to have ceased to lose weight, when the difference between the first and last weighings necessarily represents the weight of water lost by the amount of salt operated on, when heated to the degree noted on the thermometer.

When water, instead of oil, is employed for the purpose of filling the apparatus, it becomes a water-bath, and is employed for the purpose of drying substances at temperatures inferior to 212°, and is therefore extensively used in our laboratories, for the estimation of the hygrometric moisture contained in substances to be analysed.

Many of the salts which contain much water melt in their water of crystallisation when heated, and undergo what is called the watery fusion, in which state it may be regarded as being dissolved in its own water of crystallisation. Should the heat be continued, and the salt not be decomposed at the required temperature, it will ultimately enter into what is called igneous fusion, on cooling from which state it remains as anhydrous salt. Many of the anhydrous salts, when strongly heated, produce a crackling noise. Common salt NaCl, possesses this property in a remarkable degree, as may be seen on throwing a small quantity of this substance on the fire, when, if in large crystals, it will be observed to break, and in some instances to be projected to a considerable distance at the moment of each detonation. This effect is usually produced by small quantities of water mechanically retained in the cavities of the crystals, which, on being heated, is converted into steam, the expansive power of which causes the rupture of the salt. Less frequently, however, this phenomenon is occasioned by the imperfect conducting power of the salt itself, which, causing an unequal expansion among its particles, rapidly effects their division, and ultimate reduction to the state of fine powder.

**Solubility of Salts.**—The study of the solubility of salts is one of the most useful and interesting branches of chemical research, as by far the greater number of methods employed to effect the separation of this class of bodies is founded on their relative solubility in water. Many of the salts are also to a certain degree soluble in alcohol and pyroligneous spirit; but this property is chiefly confined to such as are extremely soluble in water. The solubility of a salt varies with the temperature at which the experiment has been made; and it is therefore necessary, when investigating this subject, to make separate determinations for the several points of the thermometric range.

In order to ascertain the solubility of a salt at a given temperature, it will be first necessary to obtain a saturated solution at that temperature. This may be effected in two different ways. The usual method of conducting the experiment is to add a portion of the dissolving liquor to a great excess of the salt to be examined. and having heated the mixture for at least half an hour to the required point, the liquor, which by that time will have taken up all the salt which it is capable of dissolving at that temperature, may be poured off, and considered as saturated. The same result may be obtained by operating at a higher temperature than that at which the solution is to be effected, and afterwards allowing the liquor to cool down to the required point, at which it should be kept stationary for a considerable time. The salts are usually more soluble at high than at low temperatures, and it therefore follows, that on cooling a solution saturated at a higher point of the thermometric range to one which is lower in the scale, a certain portion will be deposited in the solid form, whilst that quantity only will remain in solution which corresponds to the point to which the liquor has been cooled. Experiment proves that, with careful manipulation, these methods lead to results perfectly identical; but, unless great care be taken to prevent errors, the second process is apt to be fallacious. This arises from the circumstance that solutions of salts which are more soluble in warm than in cold water possess the property, when cooled down, without being in contact with crystals of the salt which they hold in solution, of retaining a larger portion of solid matter than the normal amount corresponding to that temperature. This inconvenience may, however, be obviated by the introduction of a small crystal of the salt operated on into the saturated solution, which will determine the elimination of the redundant salt, and deposit it in a crystalline form.

To determine the solubility of a salt at a given temperature, it is necessary to ascertain the weight contained in a solution saturated at the required point. This may be done by evaporating with proper precautions about 1000 grains of the solution to dryness in a platinum capsule. On first weighing the capsule and residue together, and afterwards deducting the weight of the capsule from the sum, the amount of dry salt contained in this quantity of the solution will be found.

If, then, we call W the weight of the solution submitted to evaporation, and w the weight of anhydrous salt found, (W-w)will be the weight of the water present. A weight represented by (W-w) of water, will then dissolve a weight, w, of anhydrous salt: consequently, 100 parts of water will dissolve, at a known temperature, T, a quantity of anhydrous salt represented by

W - w

If the crystallised salt contains water of crystallisation, it

becomes a question as to what quantity of water, at a given temperature, T, will dissolve a stated weight of the crystallised salt. Let  $\pi$  be the weight of water of crystallisation combined with the weight w, of anhydrous salt to form  $(w+\pi)$  of the hydrated salt. Then will  $(W-w-\pi)$  represent the amount of water required to dissolve the weight  $(w+\pi)$  of the hydrated salt.

Since, then, a weight of water represented by  $(W-w-\pi)$ , will dissolve a weight  $(w-\pi)$  of hydrated salt to form a saturated solution at the temperature T, it follows that 100 parts of water will form a saturated solution at the same temperature with the

weight  $100 - \frac{w - \pi}{W - w - \pi}$  of the hydrated crystallised salt; and thus

100 parts of the same hydrated salt will be dissolved by the weight  $W-w-\pi$ 

100 \_\_\_\_\_ of water.

20-75

It not unfrequently happens that the amount of salt dissolved in a given quantity of solution may be more accurately and conveniently determined by a chemical estimation, than by the usual method of evaporating to dryness and subsequent weighing. If, for example, it be required to determine the weight of sulphate of soda contained in a given quantity of liquor, it may be readily ascertained by adding chloride of barium to a weighed portion of the solution of the salt. The sulphate of baryta which is precipitated, after being collected on a filter and washed, is calcined and weighed, and from the result obtained the quantity of sulphate of soda originally present in the solution is easily deduced.

Let W be the weight of sulphate of baryta found; the composition of this salt is—

One "	equiv.	Baryta Sulphuric acid	•	•	•	•	76·64 40·00
"	"	Sulphate of baryta					116.64

It is, therefore, evident that a weight W, of sulphate of baryta 40 corresponds to W—— of sulphuric acid.

		116.64						
Sulphate of	E Soda	is composed of-						
One	equiv	v. of soda						30.97
"	,,	Sulphuric acid						40.00
		011.01						70.07
,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	33	Sulphate of soda	•	•	•	•	•	70.97

Consequently, the weight of sulphate of soda, which corresponds to 40 the amount W - of sulphuric acid, and therefore the weight 116.64 W, of sulphate of baryta, may be obtained by the proportion—

 $40: 70.97:: W - \frac{40}{116.64}: x.$ From which we obtain -  $x = W - \frac{116.64}{116.64}$ 

This method of determination may be used for the purpose of estimating any of the sulphates, whilst sulphuric acid can be similarly employed with regard to the baryta salts.

The solubility of the chlorides is easily ascertained by the addition of nitrate of silver, and the subsequent weighing of the insoluble chloride formed, and conversely the solubility of the silver salts may be estimated by means of the soluble chlorides.

It is a remarkable fact that many salts are more soluble in solutions of other salts than in pure water. A solution of nitrate of potash, saturated at a given temperature, is unable to dissolve a further portion of this substance at that temperature; but if a little common salt be added, another portion of the nitrate is dissolved. The solubility of nitrate of potash is, on the contrary, weaker in solution of chloride of potassium than in water, and the addition of this substance to saturated solutions of nitre frequently gives rise to the precipitation of minute crystals of the latter salt.

Action of Acids on the Salts.—When the acid which is made to act on a salt is the same as that contained in the salt itself, it frequently combines with a further portion of acid, and becomes an acid salt. Thus, if an excess of sulphuric acid be added to sulphate of potash KO,SO<sub>3</sub>, the acid bisulphate of that base KO,  $2 \text{ SO}_3$ , is formed. In the same way, if a current of carbonic acid be passed through a solution of neutral carbonate of potash KO, CO<sub>2</sub>, another equivalent of that acid is absorbed, and the bicarbonate of potash KO,  $2 \text{ CO}_2$ , is produced.

If the salt is incapable of forming fresh combinations with further portions of the acid, it usually merely dissolves in the excess, particularly if the acid be mixed with a considerable amount of water.

When the acid which is made to react on the salt is different from that which is already combined with its base, decomposition takes place under each of the following circumstances. If the salt be soluble in water, and an acid be added, which, by uniting with its base, is capable of forming a compound insoluble in that menstruum, the insoluble salt will be produced, and the acid at first combined with the base will be eliminated in the free state.

When sulphuric acid is poured into a solution of nitrate of baryta, a precipitate of insoluble sulphate of baryta is immediately formed, and the nitric acid remains in an uncombined state in the liquor.

If the salts formed by the union of the base with each of the acids present are equally soluble in water, it is usually impossible to decide with which of the acids the base is combined in the solution. But if the salt formed by the second acid is less soluble than that produced by the first, the decomposition may invariably be effected by evaporating the liquor to the point at which the second can no longer be held in solution, when it is deposited as an insoluble salt, according to the law above given, as the salt is really insoluble in the liquor at the state of concentration at which it was deposited.

If sulphuric acid be poured into a solution of nitrate of potash at the ordinary temperature of the atmosphere, no decomposition will apparently take place; but if the liquor be evaporated by the aid of heat, a precipitate of sulphate of potash is obtained, that salt being less soluble than the nitrate at elevated temperatures. The nitrate of potash is, on the contrary, less soluble than the sulphate at low temperatures, as nitric acid is capable of decomposing the sulphate of that base at 32° Fah.; and it is therefore evident that the action of acids on the salts is materially influenced by the temperature of the solutions in which they are brought into contact with each other.

The decomposition of a salt by an acid is sometimes determined by the insolubility of the acid which it contains. Boracic acid, which is but slightly soluble in water, is eliminated from its combinations with the bases on the addition of one of the stronger acids to their solutions. If to a concentrated solution of borax we add either sulphuric or nitric acid, a precipitate of boracic acid, in the form of pearly crystalline plates, is immediately produced, whilst sulphate or nitrate of soda remains in solution.

All the salts may be decomposed by the addition of a less volatile acid than that which is contained in the salt itself. Carbonic acid, which is gaseous at ordinary temperatures, is but slightly soluble in water, and is therefore readily displaced by nitric acid, even in the cold, as this acid is not only a liquid, boiling at a temperature above 212° Fah., but is also extremely soluble in water. Concentrated sulphuric acid enters into ebullition at 617° Fah., and consequently has the power of decomposing the nitrates at ordinary temperatures. Phosphoric acid is still less volatile than sulphuric acid, and readily replaces it when heated with its salts: and, finally, silicic acid, which is again more stable than any of the preceding, completely decomposes the phosphates when brought in contact with them at very elevated temperatures.

When a salt containing a gaseous acid which is but slightly soluble in water is acted on by another gaseous acid possessing similar properties, and having at the same time about an equal affinity for the base of the salt as the acid with which it is combined, that acid which is present in the greater proportion will invariably eliminate the other. In this way, if a current of carbonic acid be passed for a considerable time through a solution of an alkaline sulphide, the whole of the hydrosulphuric acid will eventually be expelled, and a pure carbonate of the alkali be formed. On the other hand, if a current of sulphuretted hydrogen be passed through a solution of an alkaline carbonate, carbonic acid will be evolved, and a pure sulphide of the alkaline metal ultimately obtained.

Action of Bases on the Salts.—When a further quantity of the base which it already contains is added to the solution of a salt, it frequently happens that no chemical change ensues. This is always the case when the combined acid is incapable of forming with the base a more basic salt than that originally operated on. If to a solution of sulphate of potash we add a further quantity of that alkali, and afterwards evaporate to dryness, the original sulphate of potash will again crystallise without having combined with any further portion of the additional base. Sometimes, however, a new compound is formed. Potash, added to a solution of bisulphate of that alkali, will be found to yield crystals of the neutral sulphate of that base; and if a quantity of oxide of lead be added to a solution of neutral acetate of the oxide of that metal, a basic acetate of lead will be obtained.

When the base which is added to the solution of a salt is different from that which it already contains, decomposition, attended with the formation of a new salt, often takes place. This change is dependent on circumstances analogous to those which determine the action of acids on the salts. The soluble salts are generally decomposed when the acid added to its solution is capable of forming an insoluble compound with its base. Thus the addition of baryta to a solution of sulphate of potash determines the precipitation of sulphate of baryta, and caustic potash remains in solution. In the same way, baryta causes the decomposition of carbonate of potash when brought into contact with weak solution of that substance; insoluble carbonate of baryta is formed, and caustic potash remains in the liquor. The state of concentration of the alkaline solution has, however, a great influence on the nature and extent of the changes effected,—as on boiling the carbonate of baryta with a concentrated solution of potash, a considerable amount of the carbonate of that alkali is obtained, attended with the formation of a corresponding portion of caustic baryta.

Sometimes the decomposition is effected by the insolubility of the base contained in the salt. If a solution of potash be added to a liquid containing nitrate of copper, the hydrated oxide of this metal is at once precipitated; and the same takes place with regard to all the insoluble metallic oxides when their salts are similarly treated. It is, however, necessary to remark that the decomposition of the metallic salts by the alkalies does not entirely depend on the insolubility of the oxides of the metals, but is in all probability in a great degree influenced by the superior affinity possessed by the alkalies for the acids forming the electro-negative constituents of the salts operated on.

It not unfrequently happens that an insoluble metallic oxide decomposes a salt formed by a base which is also insoluble. Oxide of silver, added to a solution of nitrate of copper, effects the decomposition of that salt; nitrate of silver is produced, and the oxide of copper is precipitated. In this case the decomposition is not effected by the greater solubility of the oxide of silver, but is the result of the preponderating affinity of the oxide of silver for the nitric acid present in the salt.

When the base of a salt is volatile, it is usually expelled by those bases which are fixed at the temperatures by which the first are eliminated. Thus lime easily expels ammonia from its combinations; and the same effect is produced under the influence of heat by the other metallic oxides, although in many cases they are precipitated from the solutions of their salts on the addition of this alkali.

Action of the Salts on each other.—The mixture of different salts gives rise to various phenomena. Sometimes they combine, and form double salts. Sulphate of alumina combines with sulphate of potash, and forms a double salt known by the name of alum. Chloride of potassium combines with perchloride of platinum, and yields a crystalline double chloride of platinum and potassium. At other times no apparent reaction takes place between the two salts; and on evaporating the solution, the salts at first dissolved are again obtained.

More frequently, however, mutual decomposition of the mixed salts ensues, and others are produced totally different in many of their characters from those originally present.

When two neutral salts mutually decompose each other, salts are obtained which are themselves also neutral. This, with many other principles relative to the double decomposition of the salts, and the action of the acids and bases on this class of compounds, are known by the name of the laws of Berthollet, and are of constant application in the chemical arts.

Mutual action of Saline Solutions on each other.—When the solutions of the salts, which by the mutual interchange of their acids and bases are capable of producing an insoluble salt, are mixed together, this decomposition invariably takes place, and the insoluble salt is precipitated. If a solution of sulphate of soda be poured into a solution of nitrate of baryta, insoluble sulphate of baryta will be precipitated, and nitrate of soda remains dissolved in the liquor.

## NaO, $SO_3 + BaO$ , $NO_6 = BaO$ , $SO_3 + NaO$ , $NO_5$ .

In the same way, if a solution of carbonate of soda be poured into a solution of chloride of calcium, carbonate of lime will be precipitated, and soluble chloride of sodium formed.

NaO, 
$$CO_2$$
 + CaCl=CaO,  $CO_2$  + NaCl.

In order that mutual decomposition should take place between two salts, it is not necessary that by an interchange of elements they should be capable of forming an insoluble compound, but merely that they should give rise, under certain circumstances, to a salt less soluble than either of those originally brought in presence of each other. If, for example, we add a solution of chloride of potassium to another of nitrate of soda, and evaporate the mixture at a low temperature, the two proximate salts separate; the chloride of potassium crystallises out, and the nitrate of soda remains in solution. If, on the contrary, the solution be evaporated at the temperature of ebullition, a double decomposition takes place; chloride of sodium, which at this temperature is the least soluble salt which can be produced by the combination of the acids and alkalies present, is deposited, and nitrate of potash remains in the liquor, which on being decanted deposits crystals of nitre on cooling.

The insoluble salts may frequently be decomposed by boiling during a long time in solutions of those which are more soluble. This may always be effected when the base of the primitive insoluble salt is capable of forming another insoluble salt with the acid of that which is made to act upon it. Thus the insoluble salts formed by baryta, strontia, and lime,—such as the sulphates of baryta and strontia, and the phosphates and arseniates of baryta, strontia, and lime,—are decomposed by boiling with a solution of carbonate of potash or soda. The carbonates of baryta, strontia, and lime, are formed, and the alkaline base remains in solution, combined with the acid of the original insoluble salt operated on. It is, however, necessary to employ a large excess of the alkaline carbonate to effect this object, as otherwise the decomposition will be found to be incomplete. If, instead of making the salts react on each other in the state of solution, they are fused together by the aid of heat, this decomposition will not only take place with greater rapidity, but the operation will also be found to have more completely succeeded than in the former case. When this latter method is employed, the fused mass should be subsequently treated with water, when the soluble salt will be dissolved, whilst that which is insoluble may be separated by filtration.

Action of Salts on each other by the dry way.—When the salts formed by the combination of the same acid with two different bases are strongly heated together, it frequently happens that they combine in definite proportions, forming a double salt, which crystallises during the cooling of the mass. In this way many of the double-silicates are obtained, which are not only found to be combined in definite proportion, but also to correspond in every respect to those produced by the hand of Nature.

The double chlorides, and many other double salts, may be produced in the same way; but it often happens that in attempting to obtain them afterwards in a state of solution, decomposition again takes place, attended with the reproduction of the original salts. If two salts formed by the union of two different acids and bases are heated together, and are, by the mutual exchange of their acids and bases, capable of forming a salt more volatile than either of those originally present, this circumstance usually determines the formation and elimination of the more volatile compound. When chloride of ammonium is heated with carbonate of lime, chloride of calcium and carbonate of ammonia are formed, which is a salt far more volatile than either of those originally present, and consequently escapes in the form of vapour, while the chloride of calcium remains in the crucible. For the same reason, if chloride of calcium be heated with sulphate of ammonia, chloride of ammonium is driven off, and sulphate of lime is left. It moreover frequently happens that the reactions obtained by strongly heating a mixture of two salts in the dry way yield results exactly the opposite of those found by the humid treatment of a mixture of the same compounds. Thus it has been just stated that on heating a mixture of chloride of ammonium and carbonate of lime, carbonate of ammonia and chloride of calcium are produced; whilst, on the contrary, a precipitate of carbonate of lime is obtained by pouring a solution of carbonate of ammonia into one of chloride of calcium. In the first case, the decomposition is effected by the volatility of the carbonate of ammonia; and in the second instance by the insolubility of the carbonate of lime.

# CRYSTALLOGRAPHY.

(49)

A SUPERFICIAL observer, on examining the various solid bodies met with in the mineral kingdom, will be inclined to consider their numerous and different forms as the result of chance, and will fail to observe among the profusion of crystals which everywhere present themselves any fixed laws more or less affecting the conformation and determining the structure of the whole. On a more attentive inspection, however, it will be found that the greater portion of them are susceptible of assuming, under certain circumstances, regular geometrical forms, which are perfectly identical in the various specimens of the same species; and that many substances that present in their exterior appearance no evidence of crystallisation, expose, when broken, a distinctly crystalline structure.

These rudimentary crystals are frequently so small as not to be distinguishable without the aid of a lens; and we may consequently infer that others exist so exceedingly minute as altogether to escape our observation.

By far the greater number of mineral bodies possess this crystalline structure; and there are but few substances which, under favourable circumstances, do not evince a disposition to assume a crystalline form.

The larger proportion of the compounds which we produce in our laboratories are capable of crystallising, or, in other words, of assuming the above-mentioned regular geometrical forms; and it is further observed that when these are produced under precisely similar circumstances, those obtained from the same substance are in every respect identical. This property of crystalline bodies affords a ready means of classifying mineral substances, and often lends its aid to the chemist in determining their true constitution.

The forms assumed by the different minerals and salts occurring in nature appear at first sight infinitely variable, and independent of all fixed principles : but by attentively studying a great number of crystals, and their progressive derivations, certain laws have been discovered which materially reduce the number of ultimate forms.

1stly. All these polyhedrons are terminated by plane faces.

2dly. These faces are systematically arranged, with regard to each other, and to imaginary lines called axes.

In the square prismatic system, for example, the two bases are perpendicular to the principal axis, whilst the other faces are parallel to that line.

In pyramids the faces are all equally inclined on the axis.

3dly. The faces of crystals are for the most part parallel two to two.

4thly. The angles of crystals are always projecting, and never retreating.

These general laws sometimes present apparent anomalies; but a slight examination of the seeming exceptions is usually sufficient to discover their causes.

It is frequently observed in the diamond that its faces are a series of curved planes. This is mostly occasioned by the great number of modifications existing on the various angles and edges of the crystal, and which give at first sight a curved appearance to the different lines which bound the solid. Sometimes, however, the faces of the diamond are in reality formed of curved planes; but this probably arises from the peculiar circumstances under which the crystal was formed, and which apparently did not permit of it taking its normal extension in certain directions.

This convexity, although peculiar to some particular specimens, in no way affects others of the same species,—as, although crystals of the diamond are sometimes found having somewhat of a spheroidal form, yet a vast many more are met with which are bounded by plane faces; and we therefore find that the rounded specimens are the exceptions, and not the rule, and may consequently be regarded as a sort of deformity of the original crystal.

Many crystalline minerals and mineral salts afford examples of apparently retreating angles. The crystals of peroxide of tin present this appearance so frequently, that its occurrence affords one of the best characteristics by which to recognise that mineral.

On careful examination, however, it will be found that those crystals which appear to have retreating angles are not in reality the crystal, but two; and that the indented angle is merely the result of the meeting and impenetration of two individuals, giving rise to a compound crystal. The plane of junction of the two crystals is usually parallel to one of the faces of the simple crystal, or to one of its diagonal planes.

**Cleavage.**—Crystals, on being struck with any hard substance, divide with greater facility in certain directions than in others; and this property, which is called their cleavage, is often made use of to expedite the cutting and grinding of the precious stones for the purposes of ornament. The cleavage of crystals, like their forms, is regulated by certain general laws, which, although less absolute than those of crystallisation, are nevertheless of great assistance in distinguishing the various substances which exhibit this property.

1stly. In the same mineral, the cleavages are always disposed in a similar way, and form angles having a constant value between themselves, as also with the faces of the crystal.

2dly. When a crystal presents cleavages in three different directions, they constitute by their reunion a solid, which constantly exhibits the same angles for the same species, and therefore affords a ready means for their recognition.

3dly. When a mineral possesses more than three cleavages, they are divided into two classes. The one is known by the name of principal, and the other of supplementary cleavages.

The supplementary cleavages, although not so easily discovered as the principal, nevertheless act an important part in the classification and distinction of the substances which possess that property. They are usually placed parallel to certain planes of the crystal,—such as those which unite a solid angle to that which is opposite.

4thly. In the same substances, the cleavages are ordinarily not equally distinct, and this distinctness has itself a certain relation with the nature of the faces of the crystal.

For instance, the cleavage which exists in the direction of the base in crystals belonging to the square prismatic system is of a different order from those which are parallel to the vertical faces, and which are both equally well defined.

If we take as an example the rhomboidal prism, fig. 4, of which each of the three faces are of a different order, its

three cleavages will also be found to be different. That which takes place parallel to the face,  $\mathbf{p}$ , is more distinct, and more readily developed, than that which follows the face, g; and this in its turn is more decided than that parallel to the face,  $\mathbf{M}$ . This relative facility of cleavage will invariably be observed in the same substance, appearing to form a species of organisation in these inorganic bodies, and at the



same time shows the intimate nature of the relation existing between the number and nature of the cleavages possessed by a substance, and the form of its crystals.

In certain minerals, such as sulphate of lime, the cleavage may be effected with the greatest ease, and transparent nacreous plates are readily separated, either by a knife, or by the use of the nail alone. This extreme facility is, however, very rare; and it seldom happens that the cleavage of a mineral can be determined without

#### CRYSTALLOGRAPHY.

the use of considerable force. The best method of doing this, is to place a chisel or some other sharp instrument in the presumed direction of the required cleavage, and then striking it with a hammer or mallet.

The cleavage of many crystalline bodies can only be determined on closely examining their structure by the aid of a strong transmitted light; on doing which, a series of parallel lines naturally drawn on the faces of the crystal will be observed. If a sharp instrument be now pressed on the surface of the crystal with its edge parallel to the direction of those lines, the cleavage may, in most instances, be readily effected by a blow struck on the back.

**Primitive and Secondary Forms.**—By extending the idea of cleavages to those minerals which do not appear to possess that property, it is easy to conceive that every crystal contains a sort of central nucleus, around which its faces are systematically placed. This central foundation, which is purely hypothetical, is called the primitive form of the crystal; and the secondary forms are those which are derived from it by the apparent modification of its angles and edges. The reunion of the laws, according to which the secondary faces are derived from the primitive form, is called the crystalline system.

Crystalline System.—It is necessary to distinguish between the crystalline system and the primitive form. The right rhombic prism, for example, is a crystalline system; but the rhombic prism, under the angle 101° 42′, is the primitive form of sulphate of baryta; whilst that under the angle 104₀ is the primitive form of sulphate of strontia.

The sulphates of baryta and strontia consequently crystallise in the same systems; but as the angles of the hypothetic radicals possess different values, their primitive forms are necessarily different.

**Governing Forms.**—Among the various forms assumed by the erystals of a mineral substance, two or three are invariably the most common, and in almost all cases communicate their general appearance to all the crystals of that body. Thus the crystals of fluoride of calcium, although frequently exhibiting very numerous modifications, possess the general forms of the cube and the octahedron, although in many instances the angles and edges are modified by almost innumerable facettes belonging to some of their derived forms. The governing forms are usually either the primitive form of the crystal, or one or two of its more simple modifications, although some instances occur in which their derivations are much more complicated.

The terms employed in the description of crystals are the same

as those ordinarily used in geometry, with the exception of a very few, which are peculiar to crystallography.

When the base of the prism, fig. 5, is replaced by two faces,  $e^1$ ,  $e^1$ , it is said to be surmounted by a bevelment.

If, instead of two faces being placed on the base, several planes exist which intersect each other in a given point, the base of the prism is said to be terminated in a point.

When the angles or edges of a crystal present the appearance of being cut away, and are replaced by plane faces, which, nevertheless, do not affect the general form of the body, they are said to be trun-

cated, and the crystal is then in a sort of transition state from the governing form to another more or less complicated.

Laws of Symmetry.—These laws, which were first discovered by Haüy, regulate the passage of crystals from one form to another. According to these laws, if a modification exists on any part of a crystal, the same modification should present itself in all its other

similar parts. The figures 6 and 7 will serve to explain this idea. Fig. 6 represents a six-sided regular prism, which is composed of three distinct kinds of elements.

1stly. Twelve horizontal edges belonging to the base,

equal among themselves, and similarly situated with regard to the axis of the crystal.

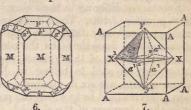
2dly. Twelve solid angles disposed in the same manner.

3dly. Six vertical edges.

The twelve angles and twelve edges of the base are replaced by two series of facettes, so disposed that those marked  $b^1$ , placed on the horizontal edges, form equal angles with the base, whilst the facettes  $a^1$ , placed on the angles, are also similarly disposed.

It will be remarked that the vertical edges of the prism, which belong to a third order of elements, have not been modified, although this might have occurred by the application of a third order of facettes.

The cube, fig. 7, offers another example of the laws of symmetry. Its six faces are placed tangentially on the six solid angles of the octahedron; and the angles which they form with the faces of the polyhedron have all an equal value. In fact, the modification which takes place in crystals, being the result of certain forces





which oblige the molecules of which the body consists to assume a crystalline form, it follows that they should act in the same manner on similar parts of the same crystal.

**Hemihedral Crystals**.—These laws sometimes present certain apparent exceptions. Thus the crystals of boracite, which crystallise in the cubic system, are only modified on each of their alternate solid angles. Haüy remarked that this property had a constant relation with the electro-polarity of the crystal, and concluded that those angles which correspond to the poles of the crystal were not modified. This supposition would seem to be verified with regard to the tourmaline and silicate of zinc; but iron pyrites, and some other minerals which are not possessed of electric properties, present the same anomaly.

Of the Crystalline Systems and their Various Modifications.— The same mineral frequently assumes various, and sometimes very dissimilar forms; but all substances identical in their chemical composition are found in forms derived from the same crystallographic radical.

Substances differing in their chemical composition possess distinct primitive forms. These forms are, however, not unfrequently analogous, and only differ from each other in the measurement of their angles. Sometimes, on the contrary, they differ entirely in the arrangement of their planes, edges, and angles, and in this latter case are said to belong to different crystalline systems. These systems are six in number, and comprehend every description of crystallised body which can possibly occur, either in nature or in the laboratory of the chemist.

According to the definition which has been given of a crystal, it is necessary that its faces should be systematically arranged, either wholly or by groups, around an imaginary line called an axis. In order, then, to establish the number of crystalline systems, it will be sufficient to discover the different arrangements which may be assumed by planes obeying the laws of symmetry around three axes which cross each other in a given point in space.

We may, in the first place, suppose that, the three axes intersect each other at right angles; or one of them may form a right angle with the two others, which may themselves intersect at an oblique angle. Again, an axis may be perpendicular to one only of the other axes, which, as in the preceding instance, intersect at an oblique angle. And, lastly, the whole three axes may intersect each other in an oblique direction.

The lengths of these axes must, moreover, be either equal or unequal; and from hence arise the six different relations corresponding to the six crystalline systems.

### 1ST. RECTANGULAR AXES.

Case 1. The three axes of equal length.

. 2. Two axes equal, and the third unequal.

" 3. All three axes of unequal length.

# 2ND. OBLIQUE AXES.

Case 1. The three axes of equal length.

" 2. Two axes equal, and the third unequal.

" 3. All the axes of unequal length.

The crystalline systems which correspond to these different relations are—

# I. The cubic.

II. The right square prismatic.

III. The rectangular prismatic.

IV. The rhombohedral.

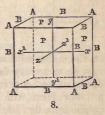
V. The rhomboidal oblique.

VI. The doubly oblique.

## 1ST. CUBIC SYSTEM.

The Cube is formed of six equal squares, each of which may be taken as its base. All its solid and plane angles are right angles. It is composed of two distinct sorts of elements,—viz., eight solid angles; twelve edges formed by the meeting of two planes. Each of the angles of a cube is at the same distance

from a central point determined by the intersection of the diagonals connecting its opposite solid angles. The twelve edges and six faces are similarly arranged. It follows from B this circumstance that the figure is perfectly symmetrical, and will admit of a series of circles being drawn, either tangentially to its sides or edges, or passing through its eight solid angles. As the axes of the cube, three



straight lines, x, y, z, fig. 8, passing through the centre of the three planes, P, P, P, and parallel to the edges, B, B, B, may be most conveniently taken.

It is evident that each of the faces of the crystal will be perpendicular to one of these axes, and parallel to the two others; and if, therefore, we call a, their length, the faces of the cube may be represented by the expressionThe cube possesses two distinct sorts of elements, and the modifications which produce its derived forms may exist separately either on its angles or edges. They are also capable of assuming different positions.

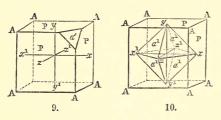
1st. The planes of the new faces may be equally inclined on the edges or angles on which the modifications take place, and in that case are said to be tangents to those angles or edges.

2d. They may, on the other hand, have different inclinations on the faces of the crystal, which meet at the modified edges or angles.

From these arrangements, two completely different classes of polyhedrons arise. In the first case, the resulting crystals are identical; in the second, they are simply regular.

### TANGENTIAL MODIFICATIONS.

**Tangential Modifications of the Angles.**—According to the laws of symmetry, when a modification takes place on one of the elements of a crystal, the same modification should be reproduced upon all its similar elements. In conformity with this principle, if we suppose that by the action of some force, of the nature of which we are ignorant, one of the angles of the cube be not deve-



loped, but is replaced by the facette,  $a^{i}$ , fig. 9, having an equal inclination on each of the three faces of the cube, each of the angles, A, will necessarily undergo the same modification, and eight precisely similar facettes will be produced

on the eight solid angles of the figure. In proportion as these new or secondary faces increase, those of the original cube will diminish, and a point will at length be attained, at which the primary form will have entirely disappeared, and the regular octahedron, fig. 10, be produced.

**Regular Octahedron.**—The inclination of each of the faces,  $a^1$ , being the same with regard to the three axes of the original cube, the resulting octahedron is regular, each of the triangles composing its plane faces being not only equilateral, but also of equal dimensions. This figure consists of two distinct elements,—viz., five quadruple solid angles; twelve edges resulting from the intersection of its planes.

Tangential Modifications of the Edges.—A plane tangentially affecting one of the edges of a cube should be reproduced on all

the twelve similar edges of that body; and consequently a figure of twelve sides, or a dodecahedron, should finally be the result of such modifications. Since the faces of this new figure are placed at equal distances from the centre of the original cube, and form, according to their construction, equal angles with its three axes, this secondary figure will necessarily be regular.

The dodecahedron is composed of 12 faces.

", ", 24 edges. ", 14 angles. Its faces are rhombs, of which the angles measure 109° 28' 16"

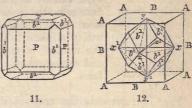
and 70° 31' 44",—the same as those of the dihedral angles of the regular octahedron.

The edges are of equal lengths.

The solid angles are unequal, and of two different kinds. Six, formed by the meeting of four planes, correspond to the angles of the regular octahedron; and eight, produced by the meeting of three planes, correspond to the eight solid angles of the cube.

The method of production of this figure from the cube and regular octahedron is the same. Its mode of generation from the cube is re-

presented in fig. 11, whilst the relative positions of its several angles and edges in relation to the elements of its crystallographic radical, are seen in fig. 12.



#### SYMMETRICAL MODIFICATIONS ON THE EDGES.

The Hexatetrahedron.—If we suppose that a face be produced on an edge of the cube, in such a way as to be unequally inclined on the base, and the vertical face placed next the observer, the laws of symmetry render it necessary that a similar plane should be produced on the other side of the same edge, in such a way that

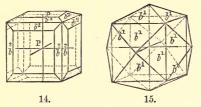
if the point B, fig. 13, represents the projection of the edge, the two faces which will be produced on it will be represented in profile by BA,  $BA^1$ ; each edge will be replaced by two faces, fig. 14, and, as the crystalline radical is bounded by twelve equal edges, the secondary solid will possess 24 faces. From the circumstance that the facettes formed on the edges of the cube may posses any given inclination it follow



13.

the cube may possess any given inclination, it follows that the number of these figures may be unlimited; but, on examination, this is found not to be the case, as nature only affords seven different crystals of this class.

The hexatetrahedron, fig. 15, pre-



sents the general form of a cube, each face of which is replaced by a pyramid with a square base. It is composed of—

24 isosceles triangles,

36 edges,

14 solid angles.

The edges are of two

kinds,—12 which are identical with those of the cube, and 24 which meet at a point beyond the axes of the cube.

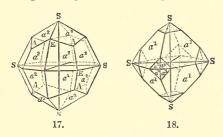
## MODIFICATIONS ON THE ANGLES.

**Parallel to the Diagonals—The Trapezohedron.**—The modifications on the angles are of two kinds; they may be either parallel to the diagonals of the faces of the cube, fig. 16, or placed



with various degrees of inclination. In the first case, the resulting solids have 24 faces, since each of the eight angles of the cube will give place to three faces. In the second, the number of modifications will be doubled, and consequently the figure will have 48 faces.

Fig. 17 represents the trapezohedron. This figure is com-



posed of—

24 faces,

48 edges,

26 solid angles.

Its faces are symmetrical, quadrilateral figures, having two kinds of sides and three species of angles; the contiguous sides being equal, as also all the

similar angles. The forty-eight edges are of two kinds; the longer, s, E, join two to two the angles of the octahedron. The twenty shorter edges, A, E, join in the same way the angles of the cube.

This form may also be produced by modifications on the eight solid angles of the octahedron, as shown in fig. 18, in which case the trapezohedron will be complete as soon as the faces of the original octahedron have entirely disappeared.

# MODIFICATIONS NOT PARALLEL TO THE DIAGONALS.

The Octakishexahedron.—In this case we have to suppose that the modifications on the angles of the original crystal are not parallel to the diagonals, and consequently each of the angles of the cube will be replaced by six new faces, fig. 19. When these have completely destroyed the planes of the

crystalline radical, a figure having 48 sides, fig. 20, will be produced. This figure consists of—

> 48 scalene triangles, 72 edges, 26 solid angles.

The edges are of three kinds: twenty-four, s, d, <sup>19.</sup> taken two and two, join the axes; twenty-four others, d,  $\Lambda$ , join together, two and two, the angles of the cube; and, lastly, the

twenty-four which remain join the angles of the octahedron to those of the cube. The solid angles are also of three kinds: six angles, s, occupy the position of the angles of the octahedron; eight others, A, correspond to those of the cube; and, lastly, the twelve angles, d, are so situated as to occupy the centre of the faces of the dodecahedron.

The different suppositions which have been made, and which amount to five in number,

embrace the principal modifications which take place on the cube and its derived forms, and show that this system, which is by far the most complicated, gives rise to but a few varieties of solid polyhedrons.

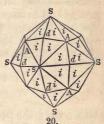
#### HEMIHEDRAL CRYSTALS.

Although it has been announced as a general law, that whenever an angle or edge of a crystal is modified, all the corresponding parts of that crystal are similarly affected, some remarkable exceptions to this rule are occasionally met with.

The cube does not afford any examples of these half crystals, since every solid body must at least possess four plane faces, whilst the cube itself is composed but of six, and therefore could not give rise to a body having half that number.

Tetrahedron.—On the contrary, one half of the faces of the octahedron are frequently wanting, and the tetrahedron, fig. 21, is thus obtained.





Pentagonal Dodecahedron.-Another very common example of these half crystals is furnished by the polyhedron, which we have

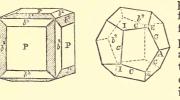
21.

described under the name of the hexatetrahe-A' dron, of which the form is that of the cube surmounted by a four-sided pyramid on each of its six plane faces.

If in this solid twelve alternate faces be suppressed in such a way that there shall be but one modification on each edge, as shown in fig. 22, in which the twelve unaffected faces are shaded, the resulting polyhedron will be com-

posed of twelve similar pentagonal planes, fig. 23.

The pentagonal dodecahedron is composed of 36 edges, which are of two kinds; six of these, a, constitute the bases of the pen-



22.



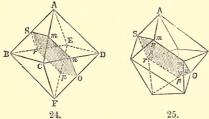
tagonal planes, and correspond by their position to the faces of the cube; twentyfour edges, c, differently placed two to two. The angles are also of two kinds: twelve formed by the meeting of three edges, A, which are irregular, and composed of angles of different values; and twelve regular angles, E,

which occupy the position of the angles of the cube.

Its opposite faces are parallel two to two.

Transposed Crystals .--- The only compound or transposed crystals belonging to this type are observed to occur in specimens of spinel, octahedral iron ore, and the diamond. In these cases the crystals consist of two half octahedrons, so joined as to give rise to a retreating angle, as seen in fig. 25.

In order to comprehend the nature of these crystals, let us suppose the octahedron, fig. 24, has by some cause been divided



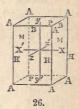
into two equal parts by the plane, m n o p r S, drawn in a direction parallel to the face, A, E, D, of the crystal. If we now imagine that one-half of the octahedron has been caused to make one-sixth of a revolution, so that the point m of the higher portion coincides with the point n of the lower, all the points,  $m n \circ r$  S, will exactly cover each other, and three projecting and three retreating angles are formed. This is precisely the appearance presented by the compound crystals belonging to this type; and the above explanation is, in a geometrical point of view, perfectly satisfactory. It is, however, impossible to say what is the real process employed by nature to effect these changes, as there is no evidence to show, and it is, in fact, very improbable, that transposed specimens ever existed as simple crystals; and consequently the only use of these suppositions will be as a sort of artificial aid to the mind in tracing out the different relations between the various crystalline forms.

In taking simple polyhedrons, such as the cube, &c., as the primitive forms of crystals, we are in like manner obliged to suppose the various modifications to have taken place on the angles and edges of the more simple bodies subsequently to their formation; whilst in reality it is most improbable that such should be the case, since crystals thus modified are found to be similarly affected even when too small to be perceived by the naked eye; and on placing them in their proper solutions, these may be made to attain a large size without in the least degree affecting the character or number of their modifications.

### SECOND CRYSTALLINE SYSTEM.

In the cubic system, the three axes around which the faces of the crystal are arranged are at right angles, and all of equal lengths.

In the present case, let us suppose that the axes are still at right angles with each other, but that one of them, the vertical axis, is variable in its length, whilst the two others remain equal. This condition destroys, to a certain degree, the regularity of the crystal, which in consequence becomes merely symmetrical: its horizontal section is a square, and its vertical a rectangular parallelogram. This solid is therefore a straight prism,



with a square base, or a right square prism, of which P, fig. 26, is the base, and M M its vertical faces.

Elements of the Right Square Prism. — In this prism the solid angles are composed of three plane right angles placed at equal distances from the centre of the crystal, and are in consequence not only equal, but also identical in their positions. These are distinguished by the letter A.

The edges are of two kinds-

Eight horizontal, B, not only of equal lengths, but placed at the

same distance from the centre, and consequently all modified at the same time.

Four vertical edges, which differ from those of the base, and all similarly placed around the vertical axis. These are consequently of the same kind, and are represented by the letter H.

It follows from these relations that the right square prism is subject to three distinct kinds of modification.

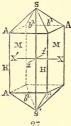
Let a be the length of the eight equal edges, and b the length of the four which are vertical.

As the relative lengths of these two distinct elements of the solid are perfectly undetermined, it necessarily follows that an infinite number of right square prisms may exist; and it is precisely this difference of relation between the edges marked B and those marked H which serves to distinguish the different substances erystallising under the form of the right square prism.

The base, P, will intersect the vertical axis at a distance h, and will be parallel to the two which are horizontal. With regard to the vertical faces, precisely the reverse of this will occur, and consequently their expressions are—

For the base, P, . . . . .  $\infty a : \infty a : h$ . For the faces, M, . . . .  $a : \infty a : \infty h$ .

**Modifications on the Edges of the Base**.—From what has been said relative to the laws of symmetry, it is evident that if one of the edges of the base of the right square prism be modified, all the



others must necessarily be affected in the same way, and the solid, fig. 27, will be produced, which, when the planes,  $b^1$ , have become fully developed, will appear as a symmetrical octahedron. A series of octahedrons can be thus produced, since the different inclinations which may be assumed by the planes,  $b^1$ , will continually vary the height of the crystal; but in all cases its section parallel to the two other axes will produce a square.

27. Modifications on the Vertical Edges.—If these modifications are tangential, a second right square prism is produced, as seen in fig. 28. When the modifying planes are, on the contrary, applied obliquely to the edges of the crystal, the eight-sided symmetrical prism, fig. 29, is the result.

**Modifications on the Angles.**—When the direction of the modifying planes is parallel to the diagonal of the base, a series of octahedrons, of which the edges of the base are parallel to the diagonals of the base of the original prism, is produced. If these secondary faces are combined with those of the primitive solid, the resulting figure is a rhomboidal dodecahedron, in which some of

the faces belong to the original crystal, and the eight others are A the result of the octahedral modification. When the secondary faces are not parallel to the diagonals of the base of the primitive solid, a double plane is produced on each solid angle, and a figure of sixteen sides is ultimately obtained, presenting the appearance of two eight-sided pyramids joined by their bases.

It is remarkable that nature presents no example of perfect

crystals of this description, although they are frequently met with in combination with other forms in the zircon, idocrase, and peroxide of tin. Its most common appearance in the zircon is that indicated, fig. 30, in which the faces,  $a^2$ , are those of the new solid.

The most frequent examples of half or hemihedral crystals offered by this system occur in copper pyrites, which is often found crystallised in the form of tetrahedrons.

### THIRD CRYSTALLINE SYSTEM.

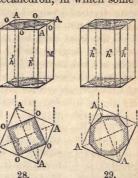
We have again in this case the three axes placed at right angles to each other, but all of unequal lengths. The solid which results from this arrangement is a straight prism with a rectangular base, fig. 31.  $A_{B}A$ 

This crystal is composed of four edges on each A base—two long, B, and two short, D.

It consequently follows that the rectangular system possesses four distinct elements—three kinds of edges, and one kind of angles—each capable of separate modification, and necessarily affecting the secondary forms assumed by the crystal.

The notation of the different faces of the prism will be-

For the base, P, . . . . .  $\infty$  b :  $\infty$  c : h. , M, . . . . . b :  $\infty$  c :  $\infty$  h. , T, . . . . .  $\infty$  b : c :  $\infty$  h.









H

T

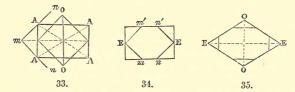
**Modifications on the Edges.**—In this prism, since the vertical edges are all situated at equal distances from the axis, they should apparently be all subject to modification at the same time. This is, however, not the case; for inasmuch as the faces, M and T, are not of the same kind, the modifications which may take place on the vertical angles, arising from the intersection of these two planes, are not necessarily double.

When modifications take place on the edges, H, in such a way that the new planes produced are parallel to the diagonals of

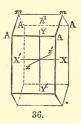


the original crystal, the right rhombic prism, fig. 32, is formed, which is by many mineralogists itself taken as the primitive form from which they derive the right square prism. The circumstance of the laws of symmetry not exacting a return of the facettes in the modifications which take place on the vertical edges of this solid, allows of the production of various prisms of four, six,

<sup>32.</sup> and eight sides, the derivation of which will be readily understood by reference to figs. 33, 34, 35.



Modifications on the Edges of the Base.—The edges of the base being of two different kinds—the one, B, long, and the other, D, short, it necessarily follows that they allow of separate modifica-



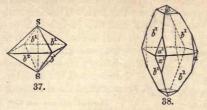
tion. If B or D be affected separately, the summit of the crystal will be surmounted by two planes, which intersecting at a given height, produce the appearance represented in fig. 36, in which the edge, B, is that supposed to be modified.

By the modification of B and D at the same time, a series of octahedrons with rectangular bases, fig. 37, are obtained, of which the heights vary with the inclination of the secondary faces on the edges of the original crystal.

**Modifications on the Angles.**—All the modifications which arise on the angles of this solid give rise to rhombic octahedrons, which differ from each other according to the inclinations of their producing planes.

It frequently happens, however, that two or more of these octa-

hedrons exist on the same crystal, as in fig. 38—a common form of the crystals of sulphur—a substance affording some of the most beautiful crystals belonging to this class.



# FOURTH CRYSTALLINE SYSTEM.

The Rhombohedron.—The three preceding classes comprehend all the solids of which the axes are placed at right angles to each other; and we now turn our attention to the consi-

deration of those of which the axes are obliquely arranged, examining also, as in the former case, the r different relations which may exist between them.

If we suppose all these axes to be of equal length, the rhombohedron, fig. 39, will be found to be the only solid fulfilling the required conditions. This figure possesses four distinct kind of elements, viz.:-

Two angles at the summit, A and A'.

Six lateral angles, E, E', &c.

Six culminating edges; three meeting at the summit, A, and the three others at A'.

Six lateral edges, arranged in zig-zag around an imaginary line connecting the solid angles  $\land \land'$ . This,

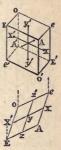
from the great symmetry of its relations with the various elements of the crystal, may be adopted as its vertical axis, but it is necessary to bear in mind that in this case the other axes will be represented by the diagonals of the hexagonal plane obtained by making a section through the crystal in the centre of, and perpendicular to, this new axis.

The notation of the faces of the rhombohedron in relation with these several axes will be—

## $a:a:\infty a:h.$

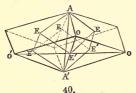
Since this solid possesses four distinct kinds of elements, it necessarily follows that the rhombohedron admits of four different systems of modifications.

Modifications on the Culminating Edges.—If these modifications are tangentially applied to the edges of the original crystal, another solid is produced, called the equi-axe, fig. 40, having the



39.

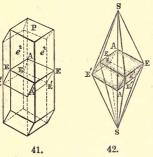
same height as the primitive solid, but a much greater lateral extension. If another plane be applied to the culminating edges of the equi-axe, another crystal will be produced, having a still more flattened appearance than the first. These crystals are very common in carbonate of lime, and this variety is frequently known as



nail-headed spar. When these modifications are unequally inclined, two distinct faces will necessarily be produced, and the resulting solid is a triangulardodecahedronorscalenohedron.

Modifications on the Lateral Edges. —If these new faces are tangents to the lateral edges of the rhombohedron,

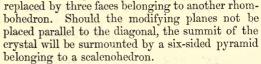
the six-sided prism, fig. 41, terminated by the planes, P, belonging to the original solid, will be produced. When, on the contrary,



the modifying planes are placed obliquely on the lateral edges of the crystal, according to the laws of symmetry, two new faces will be formed on each edge, and a new solid or scalenohedron, fig. 42, will be generated.

Modifications on the Angles of the Summits.—Tangential modifications on the angles  $\Lambda$ ,  $\Lambda'$ . These will at first produce a triangular face on the angles, which, if fully developed, generate the base of the six-sided prism above described.

If the modifications are not tangential to their angles, but are parallel to the horizontal diagonal of the crystal, they will be



Modifications of the Lateral Augles.—When the modifications on these angles are caused by planes applied tangentially to the angles, a regular sixsided prism is produced, which differs from that obtained by modifications of the lateral edges, inasmuch as the edges of the one are placed in the centre of the faces of the other.

When the secondary planes are not tangents to 43. the modified angles, two distinct facettes are produced on each, and a series of dodecahedral solids is the result.



This system offers many examples of compound and deformed crystals.

Fig. 43 is a scalenohedron of this kind, which presents the appearance of having been divided through its centre perpendicularly to its longest axis, and would seem to have made one-sixth part of a revolution around it, so that by the meeting of two dissimilar edges a series of retreating angles have been produced. This form is of frequent occurrence in specimens of dog-toothed carbonate of lime, and has also been occasionally met with in crystals of carbonate of iron from the neighbourhood of St. Austell in Cornwall.

### FIFTH CRYSTALLINE SYSTEM.

Where a crystal possesses three oblique axes, of which two are of equal, and the third of unequal length, the resulting solid will be an oblique rhombic prism, having sides of equal length, and of which the transverse sec-

tions will be rhombs.

If in fig. 44 we suppose the two axes x x', z, and z, z', which are of equal length, to be represented by a, and the vertical axis by h, the notation of each of the vertical faces will be—

$$a: \infty a: \infty h;$$

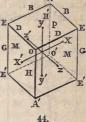
and that of the base-

# $\infty a: \infty a: h.$

In the oblique rhombic prism the sides of the base are all equal between themselves; but their relative positions with regard to the vertical axis is different. The two which unite at the angle, o, in front of the crystal, are of one kind; whilst A, E, those which meet on the back of the crystal, are of another kind.

Of the four angles, that marked o is composed, when the angles of the faces, M, M, are obtuse, of three obtuse plane angles, whilst the angle, A, on the opposite side is formed by the meeting of two acute angles and of one that is obtuse. An analogous difference would be observed in the case of the prism being acute.

The two angles, E, which are composed of equal plane angles, and of which the diagonal is horizontal, are, on the contrary, of equal value, and perfectly similar. It follows, from the nature of the oblique rhombic prism, that it possesses seven distinct elements, each subject to specific modifications, viz. :---



#### CRYSTALLOGRAPHY.

Four angles, E,—two situated on the inferior, and two on the superior base of the crystal.

Four edges, B,—two on the inferior, and two on the superior base.

Four edges, D, similarly placed.

Two vertical edges, H.

Lastly, two other vertical edges, G.

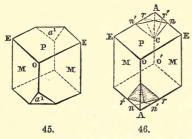
Modifications on the Angle, A.—The truncations which take place on this angle may be of three kinds,—

1stly. The projection of the modifying plane on the base may be parallel to the diagonal, E, E. This is the most common case.

2dly. The projection on the base may not be parallel to this diagonal, whilst the intersections with the lateral faces, M, are parallel to the diagonal of the face opposite the modified angle.

3dly. The whole of the secondary faces may be arranged without any parallelism with regard to the diagonals of the faces.

When the modification takes place in a direction parallel to the diagonal of the base, a simple truncation takes place on the angle, A, and a bevelment represented in fig. 45 is produced.



If the projection of the secondary face be parallel to the diagonal, E, O', fig. 46, two E modifying planes, c, n, r, and c, n', r', will, according to the laws of symmetry, be produced; and the intersection of these planes gives rise to the bevelment shown in the figure, in which the faces, for the sake of distinction, are partially shaded.

When the line c, n, is not placed in a direction parallel to the diagonal,  $\mathbf{F}$ , o', the general arrangement of the crystal, with that exception, is the same as when another bevelment is produced on the angle. It is, however, less regularly placed with regard to the elements of the original solid; and it becomes necessary, in order to express its notation, to state the distances at which the facettes intersect either the axes or the sides.

Modifications sometimes occur on the angle, o; but these are of rare occurrence.

**Modifications on the Angles, E.**—These angles being of the same kind, any modification affecting one must necessarily be reproduced on those of the same name.

The facettes formed on these angles may present the same variations as those noticed with regard to the angle, A.

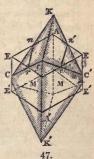
## MODIFICATIONS PARALLEL TO THE DIAGONAL A O OF THE BASE.

We will in the first place consider the modifications which take place in a direction parallel to the diagonal of the base.

Let  $c \ n \ r, c' \ n' \ r'$ , fig. 47, represent the planes of the truncations produced on the angles, E, and  $r \ n, r' \ n'$ , their projections on the base. If we now extend these planes

until they intersect in f,  $\kappa$ , we shall form a bevelment on the base which will entirely destroy it as soon as the faces, M, M, are extended so as to join the two secondary faces. Similar planes will of necessity be produced on the lower angles, E', E', and the resulting crystal, as the figure shows, is possessed of considerable symmetry.

When the modifications are parallel to the diagonal,  $\mathbf{E}$ ,  $\mathbf{A}'$ , of the crystal, the bevelment, which is produced is less symmetrical than that which is caused by the facettes, of which the projections are parallel to the diagonal; some-



times, though rarely, other planes are produced on the opposite sides; the pyroxene offers the only example of these return faces in crystals thus modified.

Analogous bevelments are sometimes produced by the modifications parallel to the diagonal, A, E', of the face on the opposite side of the crystal.

Finally, when the facettes which occur on the angle are not parallel to any of the diagonals, another species of bevelment is produced.

Modifications on the Vertical Edges.—These edges are of different kinds; the two marked H being placed at the extremities of the smaller diagonal, whilst G, G, are situated at the terminations of the larger. It follows from this circumstance that they are not at the same distance from the axis, and will consequently be separately affected.

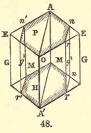
When the modifying planes are parallel to the longer diagonal, a six-sided prism, fig. 48, is produced, in which the facettes on the edges, G, have given rise to two new faces,  $g^1$ ,  $g^1$ , which, together with the remnants of the faces, M, form the new figure.

If the edges, H, had been modified in place of those marked G, another oblique six-sided prism would be produced, and two new faces, h', substituted for those above described.

In the case of modifications occurring on H and G in the same crystal, the resulting solid is a rectangular prism with oblique bases. This form is sometimes met with, particularly in the

#### CRYSTALLOGRAPHY.

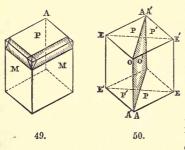
pyroxene, although it more frequently happens that the secondary faces are combined with those of the crystallographic radical; and when these are found together, an eight-sided prism is the result.



When the secondary facettes are not parallel to the diagonals, a bevelment takes place on each of the modified edges, and a prism of at least eight sides is generated.

Modifications on the Edges of the Base.—The edges of the base being of two kinds will be modified separately; but as the faces of the crystal are not of the same nature as the base, double facettes are seldom produced, and the edges are consequently merely affected with bevelments of different inclinations. The edges, B and D, are sometimes separately subject to precisely

the same changes, which are of the nature of those seen, fig. 49. When by the separate modifications of both these edges a double truncation is produced, the bases of the crystal are surmounted by



four-sided pyramids, which, on destroying the faces of the original solid, give rise to an octahedron of which all the faces are scalene triangles.

Hemitrophic Crystals.— Many crystals belonging to this class are subject to distortion or deformity. Feldspar offers a variety of examples of this kind, and is liable to two distinct species of exceptional formation.

In one case, half the crystal would appear to have made a semirevolution in the direction of the horizontal diagonal, E, E', fig. 50, when a retreating angle will be produced; and in the other, a similar movement would seem to have taken place in the direction of A, O; in which instance the external form of the crystal is not changed, but the cleavage is found to be abruptly interrupted on meeting with the plane of rotation, A, O, A', O'.

### SIXTH CRYSTALLINE SYSTEM.

When the three axes of a crystal are of unequal length, the solid is no longer possessed of the same degree of symmetry, and the figure resulting is an oblique-angled parallelogram.

All the solid angles are formed by the meeting of plane angles

of different values, and are consequently totally independent of each other. The edges of the base are also

perfectly distinct in their nature; but the vertical edges are of two kinds,—the one species marked H, and the other G.

This system contains, therefore, ten dis- <u>r</u> tinct elements, viz. :--

Four kinds of angles; Six kinds of edges.

From the number of elements subject to modification possessed by this solid, it would

appear that the changes to which it is subjected must be of a much more complicated character than those affecting the foregoing types. In reality, however, this multiplication of elements renders the comprehension of the seconday facettes exceedingly easy, as they consist of simple truncations, which are not repeated on the other faces and angles of the crystal. Fig. 52, a form belonging to axinite, may serve to illustrate this

simplicity of derivation. In this crystal four distinct elements are modified,—viz.: The angle, I, and the three edges, B, C, and H.

In some cases the opposite angles and edges are also replaced by smaller facettes, which may sometimes occasion crystals belonging to this type to be confounded with those of the preceding: but

on carefully measuring the angles and faces, they will be found to belong to separate modifications.

This type also furnishes examples of scalene octahedrons, which are produced either by the simultaneous truncation of its angles, or of the edges of the base. These crystals may, however, be easily distinguished from those belonging to the foregoing class by the circumstance of the absence of that degree of symmetry observed in those belonging to the fifth crystalline system, as their sections merely afford parallelograms, whilst two of those belonging to the former type produce rhombs.

The system of notation to be applied to the facettes produced on crystals belonging to this system, consists, as in the case of the others, in ascertaining the distances at which they intersect the several axes. But this method, which is extremely simple in the more regular types, frequently becomes very complicated in the doubly oblique prism.

### DIMORPHISM AND POLYMORPHISM.

It was for a long time believed that substances possessed of the



51.

same chemical composition invariably assumed similar crystalline forms. The progress of modern discovery has, however, shown that under certain circumstances the same substance may yield crystals belonging to two different systems. In this way carbonate of lime is found under two incompatible forms. It usually crystallises in the fourth system, and all the fragments produced by cleavage will be found to be rhombohedrons with angles of 105° 5′. Less frequently, specimens of this substance are met with which crystallise in the third system, and present cleavages totally different from those observed in ordinary calc-spar.

The form of dimorphous bodies appears to be regulated either by the temperature at which the crystals are obtained, or by the nature of the solution from which they are deposited. Sulphur, when crystallised by fusion and subsequent cooling, affords crystals belonging to the oblique rhombic system, of which the angle at the base P on M is 85° 55′ 30″, and that of M on T 90° 32′. The same substance, when obtained by the spontaneous evaporation of its solution in sulphuret of carbon, yields crystals belonging to the right rhombic system under an angle of 101° 47′ 20″. Substances which thus crystallise in two incompatible forms are said to be *dimorphous*, and the property itself is termed *dimorphism*.

When a dimorphous body is by means of abnormal influences made to assume that crystalline form which, under ordinary circumstances, is not proper to the substance, the crystals thus produced often exhibit a tendency to molecular change, which soon destroys their transparency, and ultimately causes them to crumble into powder. This peculiar transformation is very apparent in the crystals of sulphur which are obtained by fusion. When thus produced they are long prisms belonging to the fifth system, of a bright straw colour, perfectly clear, and slightly flexible. By exposure to ordinary temperatures they soon lose their transparency and become extremely brittle. If we now examine the powder by the aid of a microscope, we shall find it to consist of minute prisms belonging to the right rhombic system, so that the crystals, although still retaining externally their original form, are in reality made up of others belonging to a different system. The right rhombic prism is the crystalline type of native sulphur, as also that of the crystals of this substance when obtained from its solutions in sulphuret of carbon; and it would therefore appear probable that the natural crystals of this substance are obtained rather by the vaporisation of some volatile matter which held the sulphur in solution, than by the agency of heat and subsequent cooling.

As yet we are not acquainted with any substance that is capable

### ISOMORPHISM.

of taking more than three distinct crystalline forms, although it is easy to conceive, that, under varying circumstances, four or more different forms might be assumed by the same body, in which case this property would be distinguished by the name of *polymorphism*.

### ISOMORPHISM.

The composition of a body cannot be accurately determined by the general form of its crystals. If the substance crystallises in the cubic system, it would evidently be of little utility to say that it crystallised in octahedrons or dodecahedrons, as all the octahedrons and dodecahedrons belonging to this type are evidently in every respect precisely similar; and this description would therefore be equally applicable to every substance crystallising in the first system. This difficulty no longer exists when we consider the five other systems, as, although two different substances may crystallise in the same system, and consequently assume a very similar appearance, yet each individual will possess a separate primitive form, differing from that of all other bodies in the value of its angles, and the relation of its axes. Thus, sulphate of baryta, and sulphate of strontia, both crystallise in the right rhombic system; the former under an angle of 101° 42', and the latter of 104°. Although, therefore, these two substances crystallise in the same system, and consequently very closely resemble each other in appearance, their density and colour being nearly the same, yet in all their modifications certain relations will be observed, which by calculation may be traced to the primitive forms above given, and by these means the two substances might, in case of need, be distinguished from each other, although accurate measurements, and in some instances tedious calculation, would be required in order to do so with any degree of certainty. The difficulty of discriminating between various substances by the mere inspection of their crystals, is much increased by the fact that bodies having similar chemical relations crystallise in forms, which, although not precisely identical, yet approach so nearly to each other in the value of their angles, as not to be distinguished without great care, and the employment of good instruments. The carbonates of lime, magnesia, manganese, iron, and zinc, all crystallise in rhombohedrons. The value of their respective angles is-

Of Carbonate	of Lime		105° 5'
97	Magnesia .		107° 25'
"	Manganese		107° 20'
	Iron		107°
22	Zinc		107° 40'

From the similarity of the angles of the above substances, it is evident that a mere inspection of the crystals will not be sufficient to distinguish them from each other; and in order to do so, either accurate measurement or chemical investigation must be resorted to. It is also further observed, that substances which possess this close similarity of crystalline form, and of which the general chemical formulæ are analogous, have the property of replacing each other without materially affecting the form of the resulting crystals.

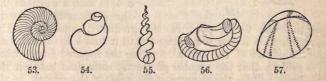
In this way the foregoing carbonates are frequently found combined in the same crystal, the angles of which will in this case be remarked to be intermediate in value between those of the crystals of the two substances which it contains, and to approach most nearly to the measurement of those of the carbonates which may happen to be present in the largest proportion. If a mixture be made of the solutions of the sulphates of iron and copper, and crystallisation be effected at a proper temperature, the resulting crystals, without being materially affected in form, will each contain a portion of the two dissolved salts. When, instead of mixing the salts in the way above described, we place a crystal of sulphate of copper in a saturated solution of sulphate of iron, a coating of the latter salt will speedily be formed on the former, and if this crystal be again placed in a solution of sulphate of copper, a coating of that salt may be formed on the layer of sulphate of iron before deposited. Substances which thus crystallise in the same system, and are capable of replacing each other in every proportion, without in any great degree affecting the form of the resulting crystal, are said to be isomorphous, and the property itself is called isomorphism.

Although substances having the peculiarity of being capable of replacing each other, without producing a change of crystalline form, are found to possess an analogous chemical composition, it does not follow that two substances having a general resemblance in this particular should be easily made to combine. If mixed solutions of the sulphates of iron and magnesia are allowed to crystallise by spontaneous evaporation, the two salts separate, and distinct and pure crystals of each will be obtained.

These salts have a similar chemical relation, and it would therefore appear, according to the rule above mentioned, that they should crystallise together in all proportions. On examining the two salts thus obtained, however, they are not found to contain a proportional quantity of water, and therefore, although in each case the relation between the acid and base is the same, yet the chemical composition of the two must not be regarded as similar, and they therefore cannot be made to crystallise together.

### PSEUDOMORPHISM.

It sometimes happens that by the agency of certain forces, crystals undergo a change of composition without their form being in the least degree affected. In this way we find spinel change into steatite, and iron pyrites into red or brown iron ore. We also frequently observe that cavities once occupied by crystals of feldspar become filled with peroxide of tin, or that crystals of quartz have been, as it were, moulded in the cavities once occupied by fluoride of calcium. It is extremely difficult to understand how some of these changes take place, but the same causes do not appear always to produce the effect. Specimens of galena have been found, in which one-half the crystal is composed of sulphate of lead, whilst the other still remains in the state of sulphide. In this case the oxidation of the sulphide is evidently the cause of the difference of composition, and therefore the change cannot be ascribed to the destruction of the original crystal and the formation of another body in the mould left. This, however, would appear to be the more frequent method employed by nature in the formation of these bodies, although it is difficult to understand what could have been the nature of the forces by means of which the substances composing the original crystal have become removed. The pseudomorphous crystals of quartz and oxide of tin are, however, evidently casts moulded in the cavities left by the destruction of other and differently formed bodies, by some agent which appears in no degree to have affected the rock in which they were imbedded, as the angles of the pseudomorphous forms are frequently as sharp as those of the original crystals. Other bodies besides crystals are sometimes replaced in the method above described, and in this way it is no uncommon occurrence to find shells, such as figs. 53, 54, 55, 56, and 57, replaced by iron pyrites.



DETERMINATION AND MEASUREMENT OF CRYSTALS.

From the circumstance that the shape of a crystal is invariably connected with, and dependent on, its chemical composition, it becomes a matter of importance not only to ascertain to what par-

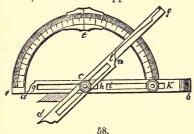
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ticular system it may belong, but also, from an accurate measurement of its different angles, to determine its primitive or distinctive form.

The system to which a crystal belongs may in most instances be ascertained by a mere examination of the nature of its modifications, although even this cannot in all cases be effected without the aid of an instrument. If, however, we require to know the characteristic form of the crystal, that is, the value and relations of its various dimensions, it becomes absolutely necessary that its different angles should be accurately measured, and in many instances trigonometrical calculations must be employed for the purpose of deducing from those relations which admit of direct measurement, such as cannot at once be thus determined.

The most essential operation, in order to ascertain the nature of a crystal, consists in measuring the inclinations of its various faces on each other, and for this purpose instruments called goniometers are employed. These are of two kinds, as the angles may be either directly and mechanically measured as by the applied goniometer, or as in the case of the reflecting instrument, the supplementary angles are those alone obtained by immediate observation.

The applied goniometer, fig. 58, is composed of a divided semicircle, to which are applied two metallic limbs, of which one, a, b,



is fixed at o on the divisions, whilst the other, d, f, which is moveable, indicates on the half circle the measurement of the angle. In order to take the measure of an angle by means of this instrument one of its faces should be applied on the fixed limb, a, b, in such a way that the edge of the angle be exactly

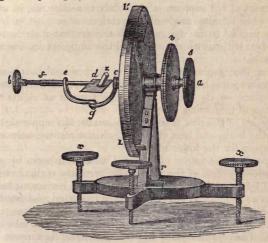
perpendicular to the plane of the graduated semicircle. The moveable limb is now to be turned until it comes in contact with the second face of the crystal, forming the required angle, when it is evident that the number of degrees comprised between the two limbs will be the measure of the angle of the crystal.

The two limbs, a b, d f, have the power of moving in the slots i k, g h, l d, in such a way as to admit of lengthening or shortening the jaws of the instrument, c a, c d, so as to adapt them to the dimensions of the crystal to be measured. Without such a contrivance this goniometer would be comparatively useless, as

instances frequently occur in which, either from the size or situation of the crystals to be measured, but very short jaws could alone be applied to them.

This instrument is, however, never used when very accurate results are required, as, in the first instance, it is extremely difficult to ensure perfect contact between the limbs of the instrument, and the faces of the crystal; and in the second, it cannot be applied to such as do not possess a considerable degree of hardness, and is consequently seldom applicable for the measurement of those which are artificially produced in our laboratories.

The reflecting goniometer is capable of affording very accurate results, but can only be employed for the measurement of crystals possessing a certain degree of polish. A great many different instruments of this kind have from time to time been recommended by mineralogists, but they are all founded on the same principles as the goniometer invented by Dr. Wollaston, and which is that most generally employed.



59.

Wollaston's goniometer, fig. 59, consists of a vertical brass circle L L' graduated on its edge, and mounted on a horizontal support,  $p \ q \ r$ . This circle admits of being turned by means of the milled-headed nut v. The vernier,  $v \ w$ , immoveably fixed to support  $p \ q$ , by a brass arm, serves to measure the number of degrees through which the edge of the circle has been made to pass.

### CRYSTALLOGRAPHY.

The axis which supports this part of the instrument is hollow. and contains another moveable rod, a c, turned by the nut s. At the extremity, c, of this interior axis, a c, is attached a universal joint, cgeb, on which the crystal, Z, is supported. This joint consists of a semicircular piece of brass, c g e, articulated at g, and having at its extremity, c, a hollow cylinder, e f, split so as to act as a spring on the rod b d, which is turned by means of the nut The rod b d is itself split at d, where a thin plate of brass is ь. inserted, on which the crystal is to be secured by a little softened wax. The crystal being thus placed on the moveable interior axis, a c, may be turned by means of the nut s, without moving at the same time the graduated circle of the instrument, or, if the nut v be employed, both the circle and crystal are made to revolve together. The various motions of which the support, c g e b d, admits, make it easy to regulate the distance between the crystal and the face of the graduated circle, as also to change its inclination with respect to the plane of the instrument. This facility of adjustment of the support is absolutely necessary, as, in order to measure the dihedral angle of a crystal, its edge must be brought exactly parallel to the axis on which the graduated circle is made to revolve: without which precaution the angle obtained would not be that of the crystal examined.

When the instrument is to be used, it should be placed on a table before some building which presents several horizontal lines well defined on its exterior, and which serve as sights in the operation of measuring a crystal.

The edge of the roof is usually chosen for the upper sight, and one of the horizontal bars of a window most conveniently answers the purpose for the lower one.

To measure the angles of a crystal we should begin by getting the graduated plate of the instrument perfectly vertical, which is effected by means of a spirit level fixed in the horizontal foot, and the screws x x x. It is also necessary that the graduated circle should be perpendicular to the front of the house, and consequently to the lines which serve as sights in the observation which is to follow. The crystal should now be fastened on its support with a little wax, softened by the addition of turpentine, and the edge of the required angle brought precisely parallel to the axis of the moveable circle. In order to do this the eye is placed very near the crystal, and in such a position that the lower sight may be seen in the direction of its edge. The interior axis, a c, is then to be turned in such a way that the eye, still retaining the same position, may be enabled to see the upper sight reflected in one of the faces of the crystal. The direction of this reflected image ought to be rigorously parallel to that of the line taken as the

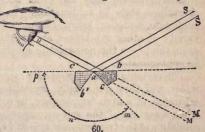
lower sight seen directly. Should this condition not be fulfilled, the crystal must be readjusted by means of the joints attached to the support, until one of its faces is found to be perpendicular to the plane of the graduated circle. If the second face satisfies the same conditions, it is a proof that the edge of the crystal is itself perpendicular to the plane of the instrument.

It frequently happens that a number of trials have to be made before the complete parallelism of the edge can be thus established: but a little practice soon enables this to be done with considerable facility.

The crystal being in this way properly placed, we may proceed to measure the angle. For this purpose 180° on the wheel should, by turning the nut v, be made to coincide with o on the vernier. The crystal is now brought in such a position that the image of the upper sight reflected on one of its faces may coincide with the line used as the second sight, seen directly. This is effected by turning the nut s, which moves the crystal without affecting the position of the divided circle LL'. We now turn, by means of the nut v, the plate LL', and with it the interior axis, a c, together with the crystal, until the eye, which should remain constantly in the same position, perceives the higher sight reflected in the second face of, and in coincidence with, the lower line chosen as a sight, at the beginning of the experiment. The angle through which the circle has moved, and which is the supplement of the angle of the crystal, is now read off by means of the fixed vernier.

In order the better to understand this, let us suppose that  $a \ b \ c$ , fig. 60, is the position of a dihedral angle when the eye of

an observer, o, perceives the image of the uppersight S, reflected on the face  $a \ b$  of the crystal, and in coincidence at the same time with the lower sight M, seen directly. It is evident that before the eye can perceive the same coincidence on the other face  $a \ c$  of the



angle, the crystal must have assumed the position a'b'c', to effect which the face a c must be made to describe the arc m n p, which will be the supplement of the angle sought, and by subtracting this from 180°, the true value of the measurement is obtained.

The reflecting goniometer affords means of measuring the angles of crystals (if they present good reflecting surfaces), to within a few minutes of error; but when this is not the case, it is sometimes found necessary to apply a piece of mica to its faces, in order to render them capable of reflecting the light with sufficient distinctness to allow the angles to be taken.

In these cases the thin scales of mica may be kept in their places, either by a little gum dissolved in water, or in some instances by water only. When this means is employed, the results can only be regarded as being approximations to the truth, and when the nature of the crystal will admit, the direct goniometer should be resorted to.

### METHODS OF OBTAINING ARTIFICIAL CRYSTALS.

The crystallisation of bodies is effected either by fusion and afterwards allowing them to cool, or by their solution and the subsequent cooling or evaporation of the liquids in which the substances are dissolved.

The metals are frequently obtained in the crystallised state by fusion. If a few pounds of bismuth be melted in a crucible, and then allowed to cool until a pellicle of solid metal begins to form on the surface, crystals may be obtained by piercing this crust and allowing the still liquid portion in the centre to flow out. On breaking the shell which remains after this operation, it will be found to be lined with beautiful crystals of bismuth belonging to the cubic system. Lead, when heated in large masses, and slowly cooled, also deposits crystals, and on this circumstance is founded one of the more recent improvements in the refining of that metal.

Many volatile salts and other bodies may be obtained in a crystalline state by sublimation. In this way calomel, corrosive sublimate, camphor, iodine, benzoic acid, naphthaline, and a vast variety of other substances, are crystallised and purified at the same time from the non-volatile substances with which they may be contaminated.

The metallic salts are generally more soluble in hot than in cold water, and they are usually crystallised by allowing a solution, saturated at a high temperature, to cool down slowly to a lower, when a portion of the salt corresponding to the difference of its solubility at the two temperatures will be obtained in a crystallised form. In order to obtain fine crystals, it is necessary that the cooling should take place as gradually as possible, as if this were rapidly effected the molecules of the substance appear not to have time to arrange themselves in accordance with their several impulses, and a deposit of the salt, in the form of a sandy powder, will be the result.

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When particularly fine crystals of a substance are required, manufacturers are in the habit of retarding the cooling of the solution by artificial means, such as surrounding the crystallisers with sawdust or some other non-conducting substance; in this way, and by placing the crystals obtained from one vessel in another containing a fresh solution of the salt, very large specimens may be obtained.

It frequently happens that a neutral solution cannot be made to yield fine crystals, and a slight excess of the acid which it contains may in most instances be advantageously added. This addition of a strong acid is sometimes found to assist the crystallisation of other substances besides salts. Thus, in the manufacture of tartaric acid, it is impossible to obtain good crystals of that substance without the addition of a small quantity of sulphuric acid to its various solutions. Light also appears to possess considerable influence on the phenomena of crystallisation, as crystals of camphor, when found on a glass vessel, are invariably observed to be attached to the side exposed to the light; and the same fact is frequently remarked in the laboratory with regard to other substances contained in the bottles on the shelves. If the solution of a salt be allowed to crystallise in a room lighted by a single aperture, the axes of the crystals will all be turned in that direction, in the same way that plants, when similarly situated, are always inclined towards the light.

Crystals are also found to form better on rough than on smooth surfaces, and for this reason a nucleus is often placed in the liquor in order to form a kind of foundation for the crystals. In this way we find sugar-candy crystallised on strings, bitartrate of potash on sticks, and sulphate of copper on wires of the same metal.

The precise form assumed by crystals of a given substance appears in a great measure to depend on the circumstances under which they are produced. Alum purified by repeated crystallisations crystallises in octahedrons; but if a small portion of an acid, or another salt, be added to the solution, modified crystals of various kinds are produced.

With nitric acid the four solid angles of the octahedron are each replaced by a face. Hydrochloric acid gives rise to the faces of the icosahedron or twenty-sided figure. Boracic acid determines the formation of cubic crystals. A few drops of the solution of carbonate of potash, or carbonate of ammonia, produce the same result. A solution of alum saturated at 212° yields, on cooling, octahedral crystals; but if the solution be made in covered vessels at a higher temperature, rhombohedral dodecahedrons and trapezohedrons will be produced. From the observations, made by M. Beudant, on the crystallisation of this salt, it is probable that the various forms assumed by crystals of the same substance depend not only on the nature of the mixtures from which they are deposited, but also on the temperatures at which their solutions were effected, and affords another reason for believing that the form of a crystal is governed by the nature of influences developed previous to the existence of the first portions of the solid produced.

# STATE IN WHICH THE METALS ARE FOUND IN NATURE—PHYSICAL PROPERTIES OF MINERALS.

SOME of the less oxidisable metals are occasionally found in the malleable or native state, although the larger number even of these are commonly associated with one or more of the non-metallic elements, such as oxygen, sulphur, or arsenic. By far the greater portion of the metals are, however, met with in combination with one or other of the three elements above mentioned, and are then said to be mineralised. The resulting compounds are called minerals, and when these can be employed in the arts for the purpose of furnishing the metals which they contain, they are known by the name of ores. Thus a copper ore, or lead ore, means any natural combination of these metals with other bodies in such proportion that the resulting compound admits of being advantageously treated for the metal it contains. Many of the metallic ores, instead of being compounds of two or more simple substances, consist of natural metalliferous salts, and of these the carbonates, silicates, sulphates, and phosphates, are among the most common examples. Among the metals occurring in nature in a free state, are gold, platinum, rhodium, iridium, palladium, silver, copper, mercury, antimony, and bismuth. The following metals are almost invariably found in combination with other substances-manganese, iron, cobalt, nickel, chromium, tungsten, molybdenum, vanadium, zinc, cadmium, lead, tin, titanium, and uranium.

structure.—Although mineral substances are occasionally met with in the form of crystals, they occur with much greater frequency in the state of masses possessing little or no trace of crystalline arrangement.

These massive minerals consist either of grains more or less minute, of leaves or laminæ, or of small columns or fibres. In the first case, the structure is said to be *granular*, in the second *lamellar*, and in the third *fibrous* or *columnar*.

When the structure of a granular mineral is rough, it is said to be *coarsely granular*, as in some varieties of marble.

When the grains are fine, it is *finely granular*, as in granular quartz : and if the grains are so excessively fine as not to be

detected, the structure is said to be *impalpable*, as in the case of chalcedony.

When granular minerals admit of being crumbled between the fingers, they are said to be *friable*.

Lamellar minerals may exist either in thick or in thin leaves; and these may also possess the property of being more or less easily separated from each other. When the laminæ are thin, and easily separated from each other, they are called *foliaceous*. If, on the contrary, they are thick, the term *tabular* is often applied to them.

The laminæ of which minerals are composed, may be *elastic*, as in mica; *flexible*, as in talc or graphite; *brittle*, as in the case of diallage.

Minerals possessing a columnar structure, are called *fibrous* when the columns are very minute and lie in the same direction, as in gypsum and asbestos.

When the fibres cross each other so as to form a kind of network, the structure is termed *reticulated*.

When the laminæ radiate from a common centre, the structure is known as *radiated* or *divergent*.

The forms of mineral substances are also frequently expressed by names derived from bodies to which they are supposed to bear a certain resemblance. Thus *reniform* substances are those possessing the shape of a kidney. When the surface of a body is made up of groups of rounded prominences, it is called *botryoidal*; or if the protuberances be of larger dimensions, the term *mammillary* is applied to it. *Filiform* means like a thread; and a parallel, needle-formed structure, is called *acicular*.

It sometimes happens that minerals occur in the form of conical masses, resembling icicles, which in many instances have a hole running through their centre. Carbonate of lime offers the most numerous examples of this kind of formation, which is commonly occasioned by the dropping of water from the roof of a cavern. In this case, the water surcharged with carbonic acid holds the carbonate of lime in solution; and when that escapes, the mineral is deposited in the solid form. The cones thus depending from the roof have received the name of *stalactites*, and are in most instances placed immediately over similar formations on the floor, called *stalagnites*, by the union of which with the stalactites above, complete pillars, from the floor to the roof, are occasionally produced. Chalcedony and brown iron ore also occur in the form of stalactites.

Substances having no regular form or structure, either crystalline or imitative, are said to be *amorphous*. State of Aggregation.—Minerals may be either brittle, sectile, malleable, flexible, or elastic.

When, on attempting to cut a mineral, portions of it are found to break off, it is *brittle*.

A sectile mineral is one from which thin pieces may be cut with a knife, but which is reduced to powder under the blow of a hammer.

A substance is said to be *malleable* when thin pieces of it may be cut off, and the portions thus separated admit of being flattened by hammering.

When a mineral admits of being bent, and is not possessed of sufficient elasticity to cause it to resume its original form when the force deflecting it is withdrawn, it is said to be *flexible*. Talc may be cited as a good example of this property.

If, after being bent, it has the power of resuming its original position, as in the case of mica, the body is said to be *elastic*.

Fracture.—Minerals are possessed of four different kinds of fracture; these are severally termed conchoidal, hackly, even, and uneven.

When a substance breaks with a convex and concave surface, as in the case of flint, its fracture is *conchoidal*.

When the elevations are sharp and uneven, as in broken iron, it is *hackly*.

If the surface is nearly flat, its structure is said to be even.

The fracture of a substance is said be *uneven* when its surfaces are subject to various elevations and depressions.

Hardness.—The hardness of minerals is sometimes employed for the purpose of distinguishing them from each other: by this means we could never fail to recognise the diamond, which has the power of scratching all other bodies. The ruby and sapphire also scratch all substances with the exception of the diamond. This test, moreover, affords an easy means of discriminating between real and artificial gems, as the extreme hardness of the one, compared with that of the other class, at once reveals their different origin. For the same reason, it would be impossible to confound crystallised carbonate of lime with gypsum, as the former is possessed of considerable hardness, whilst the latter is easily marked by the nail. These distinctions can, however, only be employed in cases where great differences exist; for as yet there is no method. known of discriminating by this means between minerals of which the hardness is nearly equal. For the purpose of better effecting these distinctions, substances of different degrees of hardness have been selected to serve as types of comparison. They are-1. Talc; 2. Gypsum; 3. Crystallised carbonate of lime; 4. Fluoride of Calcium; 5. Phosphate of magnesia; 6. Feldspar; 7. Quartz; 8.

Topaz; 9. Corundrum; 10. Diamond. In order to indicate the hardness of any body by means of the above table, it is usual to give the two numbers between which the intermediate body is placed with regard to this property; so that the hardness of the emerald would be expressed by 7—8, which means that it is harder than quartz, and less resistant than the topaz.

**Odour.**—Some minerals have the property of giving off, under certain circumstances, fumes possessed of an odour which may be employed as a means of detecting the substances which they contain.

If an ore of arsenic be rubbed until it becomes slightly heated, a distinct smell of garlic will be observed, which, on heating the substance before the flame of the blowpipe, becomes still more apparent. This odour, which is characteristic of the compounds of arsenic, is termed *alliaceous*.

When selenium or a selenide is strongly heated, a distinct smell of decayed horse-radish is perceived. This smell, which is peculiar to burning selenium, is known as the *horse-radish odour*.

The odour proceeding from burning sulphur, or the roasting of a sulphide, readily reveals the presence of that substance, and is termed *sulphureous*.

When certain varieties of quartz and lime-stone are strongly rubbed, they give off the odour of rotten eggs. This peculiar smell is occasioned by the evolution of sulphurctted hydrogen; and substances which possess this property are termed *fetid*.

Clays and other substances containing large quantities of alumina afford a peculiar odour when breathed upon; whilst a few, such as pyrargillite, present the same phenomena when heated. This odour is termed *argillaceous*, and may frequently be observed in the open air just as the ground begins to get moistened by a shower.

**Taste**.—The taste of a mineral may sometimes be employed as a means of its determination, although it seldom happens that this alone can be considered conclusive evidence of its composition.

When a substance tastes like ink, it is said to be *astringent*.

If a body, as in the case of common alum, possesses at the same time a sweet taste, it is described as having a *sweetish astringent* flavour.

The taste of common salt is usually called saline.

Tastes similar to that of soda are termed alkaline.

Tastes like that of saltpetre are described as cooling.

The acids are *sour*, and certain salts, such as the sulphate of magnesia, extremely *bitter*.

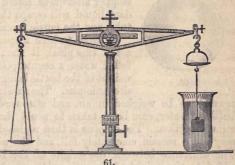
**Density of Specific Gravity.**—By the specific gravity of a substance is understood its weight as compared with that of an equal bulk of some other body taken as a standard of calculation. In the case of solids and liquids, distilled water, at the temperature of 60° Faht., is taken as this point of comparison; but the densities of the gases are usually estimated in relation to common air taken as unity.

In order to determine the specific gravity of a solid body, it is necessary to ascertain its weight when weighed in air, and also to learn how much it loses in weight by immersion in water. If we call its weight in air W, and its weight when suspended in water w, it is evident that W—w will represent the weight of an equal bulk of that liquid, as whenever a solid is placed in a liquid which covers it, it must necessarily displace precisely its own bulk of the medium in which it is situated. The specific gravity of a body being its weight in comparison with some other substance taken as a standard, it will easily be obtained from the above data, and is nothing more than the relation existing between W and W—w,

which will consequently be represented by  $\frac{W}{W-w}$ .

Hydrostatic Balance.—The most common method of taking specific gravities is by means of an ordinary balance, fig. 61, of which the pans are suspended by strings of unequal length. In

order to obtain a density by this instrument, the substance to be operated on should be attached, by a hair or filament of silk, to the shorter pan, which has a hook adapted to its under side for that purpose.



now be added in the other pan, until the equilibrium is restored; and when this takes place, the weight W will be noted as that of the substance in air. To obtain the corresponding weight of an equal bulk of water at the temperature of 60° Faht., a vessel of that liquid is now placed under the shorter pan in such a way that the suspended fragment, of which we desire to know the density, may be completely immersed in it, and weights are to be removed from the other pan, until the equilibrium be again restored.

This second weight, w, deducted from W,-that obtained by weighing the substance in air,-gives the weight, W-w, of an equal volume of water, and the required density  $\frac{W}{W-w}$  is at once

found by dividing the weight in air by the difference. In order to conduct these operations with great accuracy, it is necessary to employ a very delicate balance, and to remove any bubbles of air which may attach themselves to the substance when placed in water, by means of a feather or camel's-hair brush. The temperature of the water should also be kept constantly at 60°, and any variation of the barometer from 30 inches should be duly allowed for.

Specific Gravity Bottle .--- In cases where but small fragments of a substance can be obtained, the instrument, fig. 62, is most conveniently employed. This consists of a small bottle, of which the stopper, nicely fitted by grinding, is traversed by a capillary



tube, and is so arranged that it cannot sink beyond a line marked on the neck of the phial. By this means, it is easy to obtain a constant weight of water in the instrument, since, if it be filled beyond the line and the stopper afterwards forced into it, the redundant liquid will escape through the capillary tube, and the bottle remain exactly full.

In order to take a specific gravity by the aid of this phial, it should first be weighed full of water, a counterpoise equivalent to the weight of the bottle being placed in the opposite scale-pan. The substance to be examined

must then be weighed in air, and afterwards dropped into the bottle of water, care being taken to avoid the loss of the most minute portion. The stopper is then replaced, so that the bottle may again remain completely full, and the whole is re-weighed. The difference between the weight of the bottle of water, W, added to the weight of the mineral in air, W' or W + W', and that of the bottle of water, w, when containing the fragment to be examined, is evidently W+W'-w, and the specific gravity sought

will consequently be represented by  $\frac{W+W'}{W+W'-w}$ .

An example may probably render this explanation more easy to understand.

I find that the bottle full of distilled water at 60° Faht., and 30 inches of the barometer, weighs 995.74 grains = W.

And the substance, which is crystallised sulphate of baryta, weighs in air 62.07 grains = W'.

The bottle, with the sulphate of baryta and water together, is found to weigh 1044.02 grains = w.

The united weights of the bottle of water and the sulphate of baryta together being 1057.81 grains,=W+W', the weight of the equivalent volume of displaced water, will be 1057.81-1044.02= 13.79 = W + W' - w. It therefore follows that the specific gravity of sulphate of baryta is  $\frac{62.07}{12.79} = 4.50 =$ W+W'

W+W'-w.

A cubic foot of distilled water weighs 62.388 lbs.; and consequently the same bulk of sulphate of baryta will weigh 62.388 lbs.,  $\times 4.50 = 280.746$  lbs.

# CONSTITUTION OF THE EXTERNAL CRUST OF THE EARTH.

THE globe on which we live is made up of mineral substances of very various natures.

The aggregations of these minerals are called *rocks*, and are found to differ from each other, not only in their chemical composition, but also in their mechanical structures.

In certain rocks the minerals are arranged with a sort of general regularity. They are then said to be *stratified*, and are apparently divided into regular parallel layers, which may often be traced over a considerable extent of surface. It frequently happens that these rocks possess great facility of cleavage in the direction of their stratification, and are easily split, as in the case of roofing slates, into thin sheets. Those which possess this property are called *stratified rocks*.

Other varieties of rock do not possess this property; so that when they are divided by fissures, the cracks do not appear to follow any particular direction, but take place with various inclinations, without any appearance of symmetry. In contradistinction to the others, these are called *non-stratified* or *crystallised rocks*.

The non-stratified rocks are composed of crystalline minerals, so arranged as to resemble a mass of mineral substances, which, after being fused, had been allowed, by slow cooling, to group themselves according to their respective affinities. The result of such an experiment would be to produce a semi-vitreous mass containing various crystals disseminated in an arbitrary manner throughout its substance, and possessing no appearance of regularity in their grouping. The non-stratified rocks present precisely this appearance, and are consequently supposed to have been modified by the influence of extreme heat, from which circumstance they are also called *Plutonic* or *igneous rocks*.

The stratified rocks, on the contrary, present appearances similar to those which occur in the deposits daily taking place in the bottom of the sea, and in the beds of rivers. The vast quantities of remains of aquatic animals contained in almost all stratified rocks also renders this analogy still more striking; and geologists have therefore come to the conclusion that such deposits have been formed under the surface of water, and have consequently assigned to them the name of *Neptunian* or *sedimentary rocks*.

The deposits which occur at the bottom of seas or lakes will naturally take the form of horizontal or slightly inclined layers; and it is evident that those which occupy the lowest position are first deposited.

The different stratified rocks found in various parts of the world were probably formed in a similar way; and it therefore follows that those which are farthest from the present surface were formed previous to those above them, and that consequently the relative ages of the various stratified rocks may be at once determined by the situation which they occupy in the series. In level countries the stratifications are found lying in nearly horizontal beds; but in mountainous districts the different layers are usually very much inclined, and in some instances are even vertical.

It also frequently happens that strata possessing considerable inclination are again covered by a series of horizontal beds, which are then said to be in *discordant stratification* with relation to the former.

These appearances are evidently produced by some violent convulsion of nature, by which the beds, which were in the first instance horizontal, were forced out of their original position by the upheaving of a mass of non-stratified rock, carrying with it in its upward movement the edges of the strata on either side. If the rocks, after having assumed this position, should again become covered with water, it is evident that other beds having a nearly horizontal direction, and being therefore in discordant stratification with the upheaved portions, will be deposited.

A case of this kind is represented by fig. 63, in which, after raising the original strata to a considerable distance, the igneous



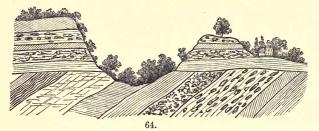
rock finally bursts through them, and appears as a granitic or trappean hill. After the expiration of a certain time, the surface has been again covered with water, and horizontal deposits have taken place, although the summit of the uplifted granite still

63.

remains above the whole. The sedimentary deposits in the immediate proximity of these masses of the primitive rocks which have thus been forced through them are usually found to be considerably changed in their structure, and the change becomes more apparent when the two rocks come into actual contact. Under such circumstances, the sedimentary deposits are found to have become to a certain degree crystalline, as if the heat produced by the injection of the melted mass of plutonic rock had so far fused the secondary strata as to admit of their several constituents arranging themselves according to their various crystalline impulses. The phenomena above described are of very frequent occurrence, and the strata thus modified are described as *metamorphic rocks*.

It is evident that the change of level produced by the irruption of the igneous rock is most apparent in the immediate proximity of the irruptive mass itself, and that they gradually subside from those points, until, at no very considerable distance, they again assume their original positions.

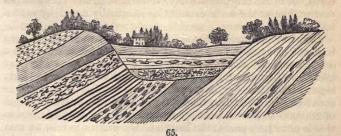
These sudden changes of level necessarily produce strong currents and eddies in localities in which the water was before in a comparative state of rest; and by this means we frequently find hollows formed by the consequent action of the water on the previously deposited strata. Fig. 64 represents a valley thus produced



by the action of a current, which, instead of depositing fresh strata, as in the case of a smooth lake, has removed those already formed, and of which the outcrop may be traced on either side of the cavity produced.

It sometimes happens that these currents, hollowing out the surface of the earth into valleys, have, by means of subsequent changes of level, again become sufficiently tranquil to allow of the deposit of fresh strata in place of those removed; and in this case new beds, fig. 65, are formed in discordant stratification with the rocks on which they repose.

Although the different strata of which the earth's crust is composed are found to succeed each other in regular order from the position of which the relative age of any particular bed may be ascertained, yet it seldom happens that any one locality possesses the whole of them without interruption. More frequently one, or sometimes several members of the series, are found to be entirely



wanting; and from this we may infer, either that the locality was not covered with water at the time that the missing strata were being deposited elsewhere, or that they were actually formed, and subsequently removed by the agency of currents, as before explained.

These breaks in the series might sometimes lead to mistakes with respect to the precise relative ages of the several rocks, did not characters of a different class lend their aid in the determination of the epochs of their formation. The greater proportion of these sedimentary deposits retain the remains, or at least the impressions left by the various plants and animals which inhabited the world at the time of their formation. These animals and vegetables differ materially in their characters, according to the position of the beds in which they are found; and as these changes are frequently very decided even in two adjoining strata of a series, the comparative study of these remains evidently places in the hands of the geologist a valuable method of ascertaining the ages of rocks.

Geologists have long sought to explain the causes which have produced the immense dislocations and upliftings above described; and although it would be here out of place to give the various theories by which these phenomena have from time to time been explained, we may, nevertheless, briefly advert to one great agent which may probably have acted an important part in producing such changes.

Geodesy teaches us that the world we inhabit is a spheroidal figure flattened in the direction of the axis of its rotation. This is precisely the figure that a liquid globe would assume if made to revolve rapidly on its axis. From this and other circumstances, it becomes probable that the earth was originally in a state of fusion, and that under the influence of extreme heat its present form was assumed. It is thus evident that its temperature would, by radiating into space, become progressively less, and also that this cooling would proceed more rapidly at the surface than towards the centre. If this supposition be correct, the temperature of the earth, even at the present day, should be greater towards its centre than at the surface; and this is actually found by experiment to be the case.

In mines, and during the sinking of artesian wells, it has been constantly observed that at a certain distance from the surface a point is attained at which the variations of the seasons in no way affect the temperature, but that beyond that point it regularly augments as the depth increases. This increase is found to be about 1° Faht. for every  $55\frac{1}{2}$  feet; and consequently at a depth of 200,000 feet, a temperature of 3,600° will be attained; and as this is not  $\frac{1}{60}$ th part of the length of the earth's radius, we may conclude that at a depth less than  $\frac{1}{60}$ th of its diameter, all the matters which compose its crust, are in complete fusion, as no substance with which we are acquainted could resist so elevated a temperature.

If we now conceive that from the cooling which takes place at the surface a contraction of the solid crust is produced, it becomes evident that the central liquid mass will become more or less compressed, and that, from being unequally restrained in its various parts, it must cause a rupture at the point of least resistance.

These eruptions will, in most instances, have dislocated the sedimentary deposits which may have been formed previous to the discharge of the injected matters; or, if this should not have taken place, they will be displaced without fracture, and produce an undulated appearance in the stratification.

From phenomena which continually occur in the neighbourhood of high mountains, it is evident that these elevations are generally due to forces thus acting from the centre of the earth towards its circumference; and from the nature of the strata traversed, geologists are enabled to establish, with great precision, the relative ages of the different mountain ranges.

From long series of investigations of this nature, we learn that several successive eruptions of great magnitude have, at distant periods, occurred on the face of the globe, giving rise to the different chains of mountains which extend in various directions over its surface; and geologists consequently class the stratified rocks into certain groups, of which the formations are supposed to be separated by the eruptions which have produced the principal mountain chains.

The rocks which constitute the exterior crust of the earth were at first divided into two classes, distinguished by the names of *pri*-

milive and secondary formations. By the former term were designated all the crystalline rocks, while the latter was collectively applied to the sedimentary deposits. It was subsequently found necessary to subdivide the secondary class into different minor groups, and for this purpose the terms transition, secondary, and tertiary, were employed. The first of these was applied to the lower stratified rocks, which, although distinctly sedimentary, still contain crystalline minerals in considerable abundance. The name of tertiary was given to the more recent stratified formations, whilst the original term, secondary, was applied to all the intermediate rocks. This method of classification was, however, found to cause great confusion of ideas, as each writer fixed the limits of the various classes in accordance with his own particular opinions; and consequently these terms are fast disappearing from geological works, and are superseded by a classification based on the relative ages of the several deposits as referred to the period of elevation of some particular mountain chain.

## OF THE PRINCIPAL KINDS OF ROCKS.

The Primitive Rocks are chiefly composed of mixtures of different crystallised minerals, of which the principal are quartz, feldspar, mica, amphibole, and pyroxene.

Quartz is merely another name for silicic acid. Feldspar is a mineral composed of the silicates of alumina and lithia, potash or soda. Mica is formed of the silicates of lime, potash, soda, and oxide of iron. Amphibole and pyroxene are both silicates of alumina, lime, and protoxide of iron.

**Granite**, which constitutes by far the largest portion of the primitive rock, is composed of a mixture of feldspar, quartz, and mica. The relative proportions of these minerals differ in the various kinds of granite, and the admixture of small portions of the oxides of iron or manganese frequently causes considerable variation of colour. The proportions in which the ingredients combine vary in the different species. Such as contain a great preponderance of feldspar are frequently described as *porphyritic*.

**Porphyry** is a species of granite in which the quartz and mica are entirely wanting, and therefore consists of a mass of feldspar containing crystals of the same substance.

Gnciss is a granite in which all the scales of mica are laid in the same direction, giving to the mass, to a certain degree, the appearance of being stratified.

**Trachytes** are the products of volcanos of very ancient date, and sometimes appear to have flowed in the form of lava, and at others to have been merely thrown up in a pasty state, as it

## 96 CONSTITUTION OF THE EXTERNAL CRUST OF THE EABTH.

frequently, on coming to the surface, gives rise to hills possessing rounded outlines. The trachytes, like the porphyries, are composed of a feldspar base, and frequently contain large imbedded crystals of that mineral.

**Basalts** are the eruptions of more modern volcanos than those giving rise to the trachytes. They are composed of a mixture of pyroxene (silica of lime, manganese, and iron), and labradorite (a kind of feldspar, containing alumina, lime, and soda). It frequently happens that when this substance reaches the surface after forcing a passage through the various sedimentary formations, it spreads out into rounded heads, and, if the conformation of the country be favourable, horizontal beds of considerable extent are thus produced. The texture of the sedimentary deposits in the immediate proximity of the fissures through which these basaltic masses have been projected is always considerably changed; and in some localities where beds of lignite have been thus traversed, they are found to be converted into coke by the intense heat evolved during the eruption.

Basalts generally exhibit a tendency to form immense columns joined together by their lateral faces. These are frequently sixsided, and, from their great regularity, present the appearance of a gigantic crystallisation, although they are in reality produced by the shrinking occasioned by the cooling of the mass after being thrown on the surface.

Lavas are the mineral substances rendered liquid by heat which flow from volcanos of the present epoch, and are generally found extended in the form of thin strata, or appear as a coating on the declivities of the mountains from which they have been ejected.

The name of *schist* is applied to minerals possessing the property of being easily separated into thin layers, and which present the foliated appearance observed in common roofing slate.

The term sand is applied to small disconnected particles of quartz.

When these grains are united by a siliceous cement, the resulting rock is called *grit* or *sandstone*. This is sometimes found of a white colour, but is more frequently stained by some metallic oxides, as in the old red sandstone, which owes its colour to the presence of peroxide of iron.

**Calcareous Rocks** are composed of carbonate of lime, and are called by various names according to their state of aggregation. In marbles and Iceland spar, it occurs in crystals: in hias limestone, it is compact; and in chalk almost pulverulent. The colours of calcareous rocks are even more various than their structures. Iceland spar is perfectly transparent; pure marble and chalk are white, whilst other varieties of this substance possess colours differing according to the nature of the organic or inorganic substances by which they are stained.

**Clays.**—The different kinds of *clay* are chiefly composed of silicate of alumina, although nearly all of them also yield traces of silicate of potash: they occur in a plastic state, and are principally remarkable for their impermeability by water. When clays contain considerable quantities of carbonate of lime, they are called *marls*.

Hydrated and Anhydrous Sulphate of Lime occurs in large quantities in the secondary formations, and is either found in regular beds, or in isolated lenticular masses.

# GEOLOGICAL DIVISION OF THE EARTH'S CRUST.

The following table, extracted from the "Geological Observer" of Sir H. T. De la Beche, shows the relative positions of the several geological formations of Western Europe, together with the nature of the various rocks of which they consist:—

# UPPER STRATIFIED, OR FOSSILIFEROUS ROCKS.

I. TERTIARY, OR CAINOZOIC. II. SECONDARY, OR MESOZOIC. III. PRIMARY, OR PALÆOZOIC.

#### I. TERTIARY, OR CAINOZOIC.

в.	Middle Tertiary Lower Tertiary	. {b. (c. . a. . a.	Pleiocene. Miocene. Eocene.	
II. SECONDARY, OR MESOZOIC.				
А.	Cretaceous Group	b. c. d. e.	Chalk of Maestricht and Denmark. Ordinary chalk, with and without flints. Merstham beds, or upper green sand. Gault. Shanklin sands, vecten, neocomian, or lower green sand.	
В.	Marine equivalents	of {b. [c. [a.	Wealden clay. Hastings sands. Purbeck series. Portland oolite or limestone.	
c.	Jurassic, or Oolitic group.	d. e. f. g. h. i. k.	Portland sands. Kimmeridge clay. Coral rag and its accompanying grits. Oxford clay, with Kelloway rock. Cornbrash. Forest marble and Bath oolite. Fuller's earth, clay, and limestone. Inferior oolite and its sands. Lias, upper and lower, with its intermediate marlstone.	

# GEOLOGICAL DIVISION OF THE EARTH'S CRUST.

D.	Trias group $\begin{cases} a. \\ b. \\ c. \end{cases}$	Variegated marls, Marnes Irisées, Keuper. Muschelkalk. Red sandstone, Grès Bigarré, Bunter sandstein.			
	III. PRIMARY, OR PALÆOZOIC.				
А.	Permian group $\begin{cases} a \\ b \end{cases}$	Zechstein, dolomitic, or magnesian limestone. Rothe todte liegende, lower new red conglome- rate and sandstones, grès rouge.			
в.	Marine equivalents of $\left\{ a \right\}$	Coal measures, terrain Houiller, Stein Kohlen Geberge.			
c.	Carboniferous lime-	. Carboniferous and mountain limestone with its coal, sandstone, and shale beds in some dis- tricts. Calcaire carbonifère, Bergkalk. Carboniferous slates and yellow sandstone.			
D.		Various modifications of the old red sandstone series.			
É.	Silurian group $\begin{cases} b. \\ c. \end{cases}$	<ul> <li>Upper: Ludlow rocks, Wenlock shale and lime- stone, Woolhope limestone.</li> <li>Middle: Caradoc sandstone and conglomerate. Lower: Llandilo and Bala beds.</li> </ul>			
	Cambrian group	. Barmouth sandstones, Penrhyn slates, &c. Va- rious rocks subjacent to the Silurian series in Wales and Ireland, and above the mica and chlorite slates, quartz, and other rocks of An- glesea and part of Caernarvonshire.			
Unknown : probably primitive.					

## OF METALLIFEROUS DEPOSITS.

Mineral deposits are of different kinds, and have received distinct names according to their various natures.

**Mineral Veins.**—The surface of the earth is in many localities traversed by clefts or fissures, probably produced by great convulsions of nature which have occurred in remote ages. These are sometimes found to be filled by the trachytic or porphyritic rocks, by the injection of which the fissures were formed, whilst in other instances they contain various metals, either in a free state, or in different forms of combination. In the former case these formations are termed dykes, but when they contain metallic ores they are called mineral veins.

It is not, however, essential, that a vein should contain a metal, as whenever a fissure has been filled with a crystalline deposit which is not of trappean origin, it is thus denominated. Mineral veins are chiefly found either in the primitive rocks, or in the transition deposits in their immediate vicinity, and in such localities the greater number of our most productive mines are situated.

Mineral veins are often nearly perpendicular in their direction, although they sometimes possess considerable inclination. Generally speaking, a vein may be regarded as a plane, of which the extension, in length and depth, is unknown, as the former is

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usually bounded by a contraction too small to induce the miner to follow it, and the latter is frequently greater than that of the deepest mines. It seldom happens that an isolated vein is found in any particular locality, and with but few exceptions, where one has been discovered, others may safely be inferred to be at no considerable distance.

It is often found that all the veins of the same locality have a nearly similar direction, and if two distinct systems of lodes should occur in the same neighbourhood, those running in one direction, if metalliferous, yield a different metal from those which do not follow the same course.

In mining districts, certain technical terms are employed for the purpose of expressing the different circumstances relating to mineral deposits; and it is therefore necessary, before entering into any details on this subject, to explain the meaning of those which are of most frequent occurrence. In the first place, the rock in which the lode is found, whatever may be its composition, is called the *country*; the veins containing the metallic ores, are *lodes*; and those which are not productive in metal, and are not in the usual direction of the lodes of the district, are called *crosscourses*; the dip, or inclination of the vein towards the horizon, is its *hade*, *slope*, or *underlie*; and its intersection with the surface constitutes what is called its *run*, or *direction*; *strings* are small filaments into which the vein sometimes splits, and of these, those which are very small, are sometimes called *threads*.

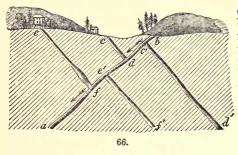
The two sides of the cavity, which contain the lode, and which consequently regulate its thickness, are called its *walls*; and if the vein has a considerable inclination, its upper boundary is termed the *hanging wall*, and the lower the *foot wall*.

Besides the productive lodes, all mining districts are traversed by others, which frequently intersect the former, nearly at right angles, but which, in the majority of cases, are not metalliferous, or, if they should contain minerals, they are seldom of the same kind as those occurring in the other lodes. The principal substances which occur in these cross-courses are quartz and clay; the quartz being mostly crystalline.

These cross-courses frequently produce *faults* or *slides* in the original lodes, which materially impede the operations of the miner, and sometimes cause large sums of money to be unproductively expended. This is occasioned by the circumstance that when two veins cross each other, the older of the two, or original lode, is almost invariably more or less thrown out of its primitive direction by the sinking or uplifting of one of the walls of the more recent vein. If the side of the cavity, in the direction followed by the miner, has sunk, the accident is called a *heave*; but if the discre-

### METALLIFEROUS DEPOSITS.

pancy has been caused by an apparent uplifting motion, the original lode will seem to have sunk, and the fracture is called a *slide*.



Thenature of these dislocations will be better understood by reference to fig. 66, in which amovement is represented to have taken place in the direction indicated by the arrows.

The sliding of the superincumbent mass on the plane of the cross-course, a

b, has caused a corresponding descent of the upper portions of the two veins, c d, e f, in the same direction, and as the lower parts, c' d', e' f', still retain their original position, the spaces c' d, e f', must necessarily occur between those portions of the lode which were in perfect coincidence previous to the rupture. In this instance it has been assumed that but one dislocation has taken place, and it will therefore be easy for the miner, after he has discovered the direction of the heave, to find the other portion of the lost lode. In order to do this, he will merely have to proceed along the course of the fault in an opposite direction to that of the arrows, by which means he is sure of finding the portion of the lode which has remained in its original position.

It, however, not unfrequently happens that, instead of one rupture, several successive dislocations have taken place, and in this case the working of the lodes in the neighbourhood is often extremely troublesome, as when the vein is once lost, it becomes a matter of great difficulty to find its continuation beyond the several faults by which it has been divided.

From what has been said of the nature of these accidents, it is evident that the veins dislocated are always more ancient than those by which their continuity has been interrupted, and consequently the study of the different systems of faults which occur in a district affords the geologist a sure means of judging of the relative ages of the mineral veins which it may contain.

The composition of mineral deposits also appears to be somewhat affected by the nature of the rock through which they pass, as certain minerals are found to exist in large quantity in the portion of a lode which passes through one kind of rock, whilst in another of a different composition they are either of unfrequent occurrence or entirely absent. As a general rule, those veins are found most productive which are situated in the immediate neighbourhood of the junction of two different species of rock. In Cornwall, from whence a large proportion of the mineral riches of this country are extracted, all the most productive mines are situated near the point of meeting of the granite and *killas*, or clay-slate.

Stratified Beds .- With the exception of the ores of iron, the metallic minerals are almost exclusively raised from regular veins, although they may sometimes occur in small quantities, disseminated in the various rocks in the vicinity of the lodes which produce them in larger amounts. The ores of iron, like other minerals, often occur in regular lodes, but are chiefly deposited either in distinct strata, as in the case of the black-band ironstone found in the coal districts, and which is often extracted through the same pits as the coal itself, or exist in irregular deposits probably produced by the infiltration of ferruginous waters, as is sometimes remarked in localities which yield the different varieties of oolitic iron-ores. These irregular masses of metalliferous ore are also, though less frequently, found to produce other metals,-such as tin, lead, or copper; but the occurrence of such deposits is generally, in the case of these minerals, considered an unfavourable indication of the ultimate value of the district for mining purposes.

Alluvial Deposits .- Besides these more ancient formations of mineral ores, it sometimes happens that the valleys in the neighbourhood of metalliferous rocks have, in the course of a long series of years, become partially filled by sands washed from the surrounding mountains, and which are found to contain a portion of the metallic riches of the hills of which they once formed a part. In some districts such deposits are extremely common, and afford, by washing, large quantities of various metals. In Cornwall, most of the valleys in the tin districts yield sands containing the peroxide of that metal. This is extracted by washing in a stream of water, when its greater density causes it to remain, whilst the lighter impurities, with which it is associated, are washed away. In the island of Banca, in the eastern Archipelago, large quantities of tin ore are thus obtained, and the extent to which such operations are carried on may be imagined, when it is mentioned that as much as 3500 tons of this metal have been annually exported from that island. The stanniferous gravels of Cornwall are seldom found immediately at the surface of the ground, but are generally covered either by a layer of other gravel, mixed with sand and clay, or by a certain thickness of peat. In order to arrive at the tin-ground, these matters are first removed, and the productive gravel, which in most instances lies immediately on the surface of the primitive rock, is then collected for washing. This method of obtaining tin is distinguished by the name of *streaming*, and the undertaking itself receives the name of a *stream-work*. The amount of tin ore annually obtained by these means is small when compared with the quantity extracted by mining from original veins; but the ore thus produced is infinitely more pure, and consequently affords a finer metal than ordinary mine tin. The principal stream-works of Cornwall are situated in the neighbourhoods of Bodmin and St. Austell, where, in connection with the mineral deposits, numerous animal and vegetable remains, such as deer-horns and hazel-nuts, are not unfrequently discovered.

From its long exposure to oxidising influences, the ores thus obtained are perfectly free from sulphur and arsenic, and for this reason are exclusively employed in the preparation of the finer varieties of grain tin. In other cases, gold in the virgin state is distributed in small grains in these sands, and this is, in fact, one of the chief sources of that metal.

The sifting and washing of such sands furnishes to Russia nearly all the gold produced in that empire, which annually amounts to about fifteen thousand pounds weight. Russia also obtains by the same means an annual supply of nearly five thousand pounds weight of platinum, which is almost entirely extracted from the streams flowing from the Altai mountains, which separate Siberia from Tartary.

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PRELIMINARY OPERATIONS.—The mineral riches of a country are frequently discovered by attentively observing the fragments brought down by the action of water from the hills into its valleys; and on tracing these to their several sources, the veins from which they were originally detached, are in many instances found. Water also acts in another way a very important part in the discovery of mineral veins, as by closely examining the faces of the different gullies and ravines, which intersect a country, a ready means is afforded of ascertaining whether its strata are traversed by metalliferous deposits; and, therefore, in exploring with a view to mineral productions, no opportunity should be lost of observing the various sections thus naturally laid bare.

If the substance of a mineral vein be harder than the rock in which it occurs, the latter is sometimes, by the alternate action of air and water, gradually removed, whilst the lode itself remains as a sort of natural hedge across the country.

A remarkable example of this kind occurs at Mouzias, in Algeria, where several lodes, principally composed of spathose iron, and sulphate of baryta, containing a small portion of disseminated grey copper, traverse a soft marly soil, which offers but little resistance to the action of water.. The rains, therefore, which are frequently very heavy in the country, have gradually washed away the softer clay, and left the outcrop of the lodes standing at a considerable height above its surface. In some places these ridges are from fifteen to twenty feet in height, and may be traced for a considerable distance across the country, intersecting in their progress all the different formations of which it is composed.

When none of the above means of observation are available, it is necessary to examine the nature of a district through the medium of artificial excavations. This is done by what is, by the Cornish miners, called *shoading* or *costeaning*. When the general direction of the lodes of the neighbourhood has been ascertained from facts elicited during the working of other mines in the district, a series of pits is sunk, as nearly at right angles as possible to the assumed run of the mineral veins. These shode pits are about three feet in width, six in length, and extend in depth

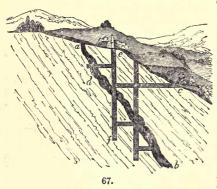
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through the alluvial deposits, a few feet into the subjacent rock. In order to avoid the chance of missing any lode which may occur in the superficies to be examined, the pits are sunk at regular distances, and afterwards united by galleries, which would necessarily traverse any vein which might escape detection by the shode pits themselves.

If the direction of the lodes in the neighbourhood is not known, or if it be uncertain whether the country be traversed by mineral deposits, it is necessary to arrange two series of pits at right angles to each other, by which means, if any occur, they cannot fail to be detected.

When a lode has been discovered, and is found to yield a metal, or presents appearances from which it may be inferred likely to prove productive at a greater depth, the first operation, if the conformation of the locality admits of it, is usually to drive an *adit level*.

This is a gallery cut a little above the surface of the nearest valley, in such a way as to intersect the lode at a certain distance from the surface, and draw the water from the higher portion of



the vein as shown in fig. 67, where the lode a, b, is traversed by the adit level c. d. Should the appearances of the vein prove favourable, a pit or shaft, e, f, is sunk in such a position, that it may intersect the lode at a proper distance from the surface, and serve as a means not only of extracting itsminerals, but also of ascent and descent to the miners employed. For this purpose, a wind-

lass or *tackle* is mounted on the shaft, and is placed on a strong stage of wood, and by the aid of this and a long rope, two buckets or *kibbles* are made to alternately ascend and descend in the pit.

Should the lode, after proper examination, be found to be productive of ore, other shafts are sunk, and a regular series of levels driven. In the first place, galleries will be excavated in the substances of the vein for the purpose of extracting its contents: these are, in the Cornish mines, placed at distances of ten fathoms from each other, and are all connected with a shaft through which the excavated rock and metallic ores are transported to the surface. Since a perpendicular shaft can only traverse the lode, which is a diagonal plane in one point, it becomes necessary that each o these levels should be connected with it by galleries perpendicular to the plane of the general run of the lode. These are called *cross-cuts*, and are usually furnished with railways for the more ready conveyance of the contents of the vein to the pit, by which they are drawn to the surface.

When, for the more convenient working of the mine, or for the purpose of ventilation, a pit is sunk from one level to another, without being opened to the surface, it is by the miners called a *winze*, and is, in most cases, made to follow the underlie or dip of the lode in which it is situated.

The water which percolates into the mine below the point at which the adit level meets the shaft, is drawn out by a series of pumps worked either by water power or a steam-engine. For a short time after a shaft has been commenced, and before it has attained any considerable depth, the rubbish removed is conveyed to the surface by a simple windlass moved by manual labour. When the pit has reached a more considerable depth, a contrivance, called a whim or gin, moved by horses, is commonly employed, although steam power is daily becoming of more frequent application. In case of steam being used, the drum of the winding apparatus is sometimes placed horizontally instead of vertically, as in the common horse whim, and flat ropes and bobbins are often employed in the place of the round ropes and cage used in the former case. These are found to be more durable and uniform in their action.

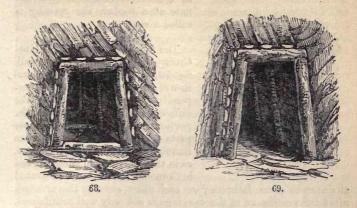
Methods of attacking the Rock.—The tools employed by the miner necessarily vary according to the nature of the rocks which he has to traverse. If the ground be moderately soft, nothing but an ordinary pick and shovel is used; but if it be hard, and is either stratified, or contains numerous fissures, he has recourse to steel wedges or points, called *gads*, by driving which into the crevices of the rock, he is enabled to split off larger portions than he could detach by the use of the pick alone. When the ground to be cut through does not admit of being thus broken, the working is effected by the assistance of gunpowder.

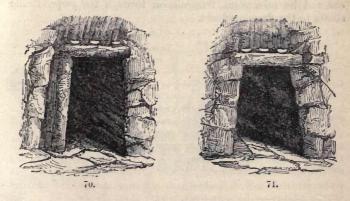
Before this agent can be employed it is necessary to bore a hole in the rock for its reception. This is done by a bar of iron furnished at one of its extremities with a steel point armed with cutting edges. To use this instrument, one of the miners holds the sharpened end of the *borer* to the rock, whilst another hits the other extremity a heavy blow with a large hammer or *mallet*. As the hole deepens, the person who holds the tool turns it between each blow about one-fourth of a revolution, and by this means a deep hole is ultimately obtained. The borer is, during the operation, from time to time removed from the hole in order to take away the broken rock, and a little water is added for the double purpose of cooling the borer and facilitating its action. When the hole has attained what is thought to be a sufficient depth, and which necessarily varies with the nature of the rock, it is carefully cleaned out with what is called a swab stick, and a proper quantity of gunpowder deposited at the bottom. For the purpose of confining this, and thereby giving greater force to the explosion, the hole is now filled up by ramming in a quantity of soft schist called *tamping*, a small hole being left by the introduction of a copper needle, which is afterwards removed, to afford means of exploding the charge when required. The ancient method of doing this was by a reed or rush filled with fine powder, which was let down into the hole and served as a channel for the spark to be afterwards communicated by a slow match, during the burning of which the miner had time to escape out of reach of the fragments of rock projected by the explosion. Recently, the rush has become superseded by the use of "Bickford's Patent Safety Fuse," which itself not only acts as a slow match, but has also the advantage both of being safer and more readily employed, as with it the copper needle is no longer necessary, the fuse being placed in the hole before it is closed, and the tamping forced in around it.

When the rock in which the hole is bored is damp from the infiltration of water, the powder is enclosed in a waterproof bag before being introduced into the cavity.

Mining Excavations .---- When a shaft is sunk, or a gallery excavated in hard rock, there will be but little difficulty in causing it to retain its original form, but should the ground be soft, and consequently offer but little resistance to pressure, artificial means must be employed for its support. This is most frequently effected by pieces of wood, although, in some instances, walls of brick or stone are employed for that purpose. Similar means are employed for the support of the various galleries or levels, and some of the different methods by which this is done may be understood from the following woodcuts. Fig. 68 represents the timbering of a gallery, all the sides of which are supposed to require support. In fig. 69, the floor being hard, is not timbered, whilst the other three sides are retained by strong woodwork. Fig. 70 represents the method of securing a gallery, of which two sides only require support; and fig. 71 shows the way in which a level with an insecure roof is sustained. When stone is employed for this purpose in the place of wood, the roof is commonly arched, but should the

floor also require support, an elliptical form is, in most instances, preferred.





**Extraction of Ores.**—The ores existing in a vein are, to a certain extent, extracted in cutting the longitudinal galleries or levels excavated in its plane, but as these are placed at considerable distances from each other, the ore thus raised forms but a very inconsiderable part of the contents of the lode. In order, therefore, to obtain the minerals between the different levels, the ore is worked out, and the space afterwards filled in with rubbish arising from the other operations of the mine, fig. 72.

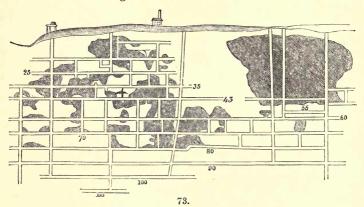
When this is done by descending from a higher level to a lower, the operation is called *stopping*, but if the excavation commences



at a lower level, and is to terminate at a higher, the opening is called a *rise*.

The following woodcut of Huel Crofty Copper Mine in Cornwall, fig. 73, will serve to give a general idea of mining operations. The perpendicular excavations show the different shafts and winzes; and the portions shaded black represent those parts of the lode which have been removed by stoping. In this mine, as in the generality of those worked in Cornwall, the levels are excavated

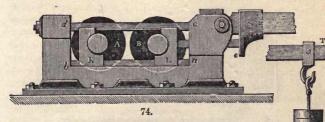
at distances of ten fathoms from each other, since by this arrangement the ventilation of the workings is not only well maintained, but every facility at the same time afforded for the removal of the ore, and its subsequent transmission through the perpendicular shafts to the dressing-floors.



Mechanical Preparation.—On reaching the surface, the ores are broken by large hammers, and divided into classes according to their relative richness in metal, whilst the unproductive portions are picked out and rejected. Few ores contain so large an amount of metal as to render their concentration by mechanical means unnecessary.

## CRUSHING AND STAMPING.

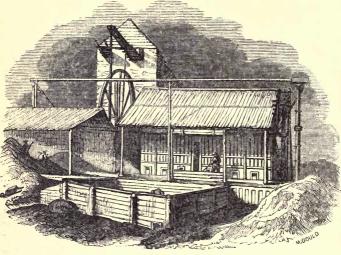
**Crushing.**—In order to reduce the fragments of mineral ores, and particularly those of copper, to a proper size, for their subsequent mechanical concentration, large cylinders of cast iron, moving in contrary directions, are frequently employed. This arrangement is represented in fig 74, in which A, B, are the crushing rollers set in motion by steam or water power: a, b, d, c,



represent a strong framing of cast iron firmly secured to a wooden framework by screw bolts. The bearings K, L, of the rollers A, B, are so arranged as to slide in grooves, and consequently admit of the cylinders

being either advanced closer together, or separated at a greater distance. To prevent accidents from the passage of large pieces of stone too hard to be broken, a certain elasticity is given to the apparatus by means of the lever, s, which by a sliding bar, and the shoulder e, constantly tends to keep the surfaces of the two grinding cylinders in contact, since its other extremity is loaded with a heavy weight, w. The ore to be crushed is allowed to fall gradually between the two rollers, through a hopper, and the weight, w, so adjusted as to suit the hardness of the mineral to be broken. On passing through the rollers, the crushed ores fall into the higher extremity of an inclined cylinder of coarse wire gauze. This being set in motion by the same power as the rollers themselves. divides the pulverised mineral into two classes, the one passing through the meshes of the trellis, and falling on the floor, whilst the other, which is too large to pass through the apertures, is carried out at the lower end of the cylinder, where it falls into the buckets of an endless chain, by which it is again brought to the level of the mill to be re-crushed.

**Stamping.** Many minerals, and especially the ores of tin, instead of being crushed by rollers as above described, are pounded into small fragments by large pestles, moved either by water or steam power. The arrangement by which this is effected is called a stamping-mill, and is represented in fig. 75, where a steamengine gives motion to an axle, not seen in the drawing, which is provided with a series of cams arranged in spirals around its circumference. Vertical wooden beams are so attached to large masses of cast iron, that when raised by cams fitted in the axle and corresponding tongues on the lifters, they fall on the mineral placed beneath them, and thus by repeated blows reduce it to a fine powder. The cams are so arranged on the spiral, that each



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lifter shall give three blows during a revolution, and as soon as the first lifter has been released from the cam, and begins to fall, the second cam in the series comes in contact with the tongue of the next lifter, and so on until each has in succession struck a blow, when the first lifter is again caught by the first cam belonging to the second system on the axle, when another series of blows is dealt by the moveable pestles. The lower portion of this arrangement, where the iron heads come in contact with the mineral to be broken, is enclosed in a large wooden trough shown in the wood-cut, in which are openings, and into these are fitted gratings made by punching small holes in sheets of very thin iron. By means of a spout, a small stream of water is allowed to flow constantly into the trough, and therefore, whenever fragments are reduced sufficiently to enable them to pass through the apertures of the gratings, they are carried off by the water into the pit, in the foreground, prepared for their reception, and where they are deposited by subsidence in a more or less finely divided state.

The size of the stamp heads, or pestles, varies in accordance with

the nature of the mineral to be broken, but their general weight is from 300 to 400 pounds. In order to attach the heads to the lifters, they are provided with wrought iron shanks, which, after being let into the end of the lifters, are kept in their places by shrinking on two strong iron bands over the wood. In some of the more modern stamping-mills, both the axles and lifters are of iron, and in this case, the upper ends of the lifters are kept in their places by iron collars, whilst the lower are fixed by keys into a mortice hole cast in the head.

Washing and Concentration of Ores.—Before describing the various processes by which this is effected, it will be necessary to understand the principles upon which all these operations are based. If we let fall from a considerable height into a liquid in a state of repose, bodies of various sizes, forms, and densities, it is evident that the amounts of resistance which they will experience in their fall will be very unequal, and that they will consequently not arrive at the bottom of the liquid at the same time. This necessarily produces a sort of classification of the fragments, which becomes very evident on examining the order in which they are deposited.

In the first instance, let us suppose that the substances have the same form and dimensions, and that they differ from each other in their densities only,—since the resistance which a body will experience in moving through a liquid medium depends entirely on its form, and the extent of its surfaces, and is in no way affected by its specific gravity : it follows that all substances will lose under similar circumstances, an equal amount of their moving force.

This loss is, however, most sensible in those substances which possess this power of movement in a less degree; or in other words it will be proportionally greater in light bodies than in those having a more considerable density. The former, for this, reason, fall through the liquid with less rapidity than the denser fragments, and must consequently arrive last at the bottom; so that the deposit will be composed of different strata, arranged in direct relation to their various densities, the heaviest being at the bottom, and the lightest at the top of the series.

If we suppose, on the contrary, that all the bodies which fallthrough the liquid possess similar forms and equal specific gravities, and that they only differ from each other in point of volume, it is evident that the rapidity of motion will be in proportion to their size, and the larger fragments will be deposited at the bottom of the vessel.

As we have supposed them, on starting, to have both the same form and density, it follows that the resistance they experience during their descent through the water, will be in proportion to the surface exposed; and as the volumes of bodies vary according

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to the cube of their corresponding dimensions, whilst the surfaces only vary in accordance with the square of the same measurements, it follows that the force of movement animating them is regulated by their cubes,  $d^3$ , whilst their resistance is in proportion to their squares,  $d^2$ , showing that the size of a body augments its descending force with much greater rapidity than the resistance offered by its surfaces.

If, lastly, we imagine that all the fragments have the same volume and density, but are of various forms, it follows that those which possess the largest amount of surface will arrive at the bottom last, and consequently, the upper part of the deposit will consist of the thinnest fragments.

It is evidently, then, of the greatest importance that the grains of ore which are to be concentrated by washing should be as nearly as possible of the same size, as otherwise, the smaller surface of one fragment in proportion to its weight, will in a measure compensate for the greater density of another grain, and thus cause it to assume a position in the series to which by its constitution it is not entitled.

This difficulty is constantly found to occur in practice, and in order to obviate it as much as possible, care is taken to separate by the use of sieves, into distinct parcels, the fragments which have nearly the same size. Although, however, the grains of ore may in this way be to a certain extent classified according to their respective dimensions, it is impossible by any mechanical contrivance to regulate their forms, which must in a great degree depend on the natural cleavages of the substances operated on, and therefore this circumstance must always in some degree affect the results obtained.

Each of the broken fragments of ore must necessarily belong to one of the three following classes:—The first class consists of those which are composed of the mineral sought, without any admixture of earthy matter. The second will comprehend all the fragments which are made up of a mixture of mineral ore and earthy matters; whils the third division may be entirely composed of earthy gangue without any admixture of the metallic ore. By a successful washing, these three classes should be entirely separated from each other. The first will form the lower stratum, and the mixed fragments follow next in succession, whilst the unproductive portion is deposited on the two other layers.

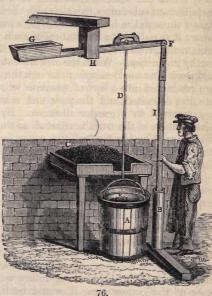
Sieve-washing or Jigging.—The fragments of ore which have passed through the crushing rollers, before described, are concentrated by being jigged or washed in sieves so as to allow each of the reduced particles to arrange itself in accordance with its individual specific gravity.

Hand Sieves .- The most ancient and simple method of effecting

this is by the hand sieve. This consists of a sieve made of perforated sheet copper, which, after being partially filled by the workman with the mineral to be washed, is placed in a large tub of water, where he gives to it a sort of undulatory motion, which causes the richer portions to accumulate at the bottom, and the earthy grains to rise on the surface. After a time he withdraws the sieve from the water, and whilst it is resting on the edge of the tub, scrapes off with a piece of thin iron, the particles thrown on the top. This is followed by a second washing and scraping, and when the whole of the absolutely worthless matter is removed, those portions which are scraped from the surface are, instead of being thrown away, collected in a heap for subsequent treatment, whilst that which is at the bottom is considered sufficiently pure for metallurgical treatment.

On the Continent, these sieves have been almost entirely superseded by the simple contrivance shown in fig. 76, in which c represents the table on which the mineral to be washed is placed.

A is a large tub of water in which the sieve E is suspended by the iron rod D, set in motion by means of the arrangement I, F, G, suspended at H, and having at the extremity G, a box for the reception of small stones to be used for the purpose of counterpoising the weight of the sieve and several fittings. By moving the rod I sliding in B, the workman gives the required motion to the sieve, and when its contents have been sufficiently washed, he removes them by the same means as when the hand sieve is employed.



A nearly similar method was formerly employed in the Cornish mines for washing and classifying the crushed ores of copper, but recently a much more effective apparatus has come into general

This consists of a large box covered with a tight wooden use. floor, in the centre of which is a circular metallic trough perforated with six holes, each about two feet in diameter, and into all these openings a sieve is closely fitted. A large piston working in a cylinder placed in the centre of this arrangement, and which is moved by an eccentric driven either by water or steam power, is made to alternately raise and depress the level of the water in the box and consequently also in the sieves, which are fixed watertight into the rings on the top of it. By this motion of the water, the particles of mineral contained in the sieves are made to arrange themselves according to their several densities, and when it becomes necessary to remove a sieve from its place, for the purpose of scraping off the less valuable and lighter portion of its contents, its place is supplied by another, which is kept ready filled to occupy the same ring when required.

Of the portions which are scraped off from the surface of the sieve, the lightest contains little or no metallic ore, and is thrown away; but the second, consisting of a mixture of gangue and metalliferous substances, together with the finely divided dust which passes through the holes of the sieves, is sent to the stamping mill, where it is reduced to the state of a much finer powder, by which treatment greater facilities are offered for its separation from earthy impurities. When the ores are not stamped dry, the water and work (fine sand) escaping through the gratings of the machine are conducted into a sort of reservoir where the heavier particles are first deposited, and the poor and consequently lighter parts are removed to a greater distance. By this process a certain classification of the work is effected, as those portions which have been carried by the force of the water beyond a given point are collected in a separate basin from those which have not arrived so far from the stamping mill.

The methods of washing and preparing metalliferous sands varies according to the nature of the minerals treated, and also depend in some measure on the localities in which they are raised, as the same ores are frequently managed very differently, and yet each method may afford equally good results. It is, however, necessary to observe, that many minerals, and particularly the ores of tin, are found so disseminated in the veins in which they occur, that it is necessary to reduce them at once under the stamping mill, since, if the crushing rollers were resorted to as in the case of the copper ores, it would be impossible to free them sufficiently, by that means, from the siliceous and other impurities with which they are contaminated.

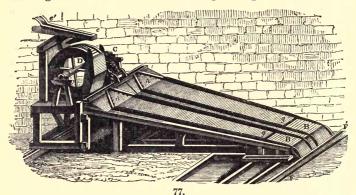
The form of apparatus employed for washing the reduced ores from the stamping mill depends in a great measure on the nature of the mineral treated, and also varies according to the locality in which the mine happens to be situated. On the Continent, the concentration is chiefly effected in three different kinds of apparatus,—the German chest, "caisse à tombeau:" the sleeping table, "table dormante," and the percussion table, or "table à secousse."

The German Chest consists of a long box placed in a slightly inclined position, and having in its lower end a series of holes, closed by wooden pegs. At its higher extremity is placed a sort of raised platform, on which the substance to be washed is deposited, and on this a small stream of water is allowed to play. By this arrangement the finer portions of the mineral are carried off in suspension in the water, and are deposited at distances from the head of the pit which vary in accordance with their several specific gravities. When the body of the chest has become full of water, the stream on the platform at its head is turned off, and one of the pegs in the lower extremity being withdrawn, the water, and lighter particles which it holds in suspension, are drawn off into reservoirs, where the solid matter is allowed to subside. As the chest gradually becomes filled with the deposited sand, a higher peg is removed, and finally, when the pit is entirely filled with the ore, the uppermost peg is alone withdrawn. The matters deposited in this way are divided into three classes. The first and heaviest is situated nearest to the head of the pit, and consists of the mineral so far concentrated as to be frequently fit for smelting without further preparation. The second and third portions, which are much less rich, are reserved for further treatment, either by the percussion table, the sleeping table, or by a second washing in the German chest.

**Siceping Tables,** which are also called twin tables from being commonly associated in pairs, consist of two inclined planes,  $\Lambda$ , B, fig. 77, varying from twenty to twenty-five feet in length, and provided with raised sides for the purpose of retaining the water which runs over their surface.

At the upper end, A, of these tables, is placed a triangular plane, which has a much greater inclination than the surfaces of the tables themselves. At the apex is an opening by which the water which holds the mineral to be washed in suspension, falls on the inclined plane: and below this, at the head-board of the table, are placed numerous triangular pieces of wood so disposed as to cause a uniform flow of water over all its surface. The mineral to be washed is placed in a small trough, c, into which a stream of water is constantly made to flow. Here the pounded ore is continually agitated by the arms of a stirrer, set in motion by a small water-wheel, D, worked by a stream of water flowing through the channel e e'.

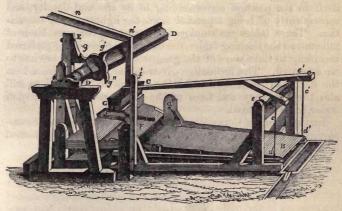
By this apparatus, the mineral is stirred up with the water, and entering on the head of the table through the aperture at A, flows



to a greater or less distance down the inclined plane. As the wooden head of this arrangement is very much inclined, no deposit can take place upon it, and consequently the whole of the pounded ore goes on to the table itself, where the richer portions remain nearest the triangular platform; whilst the poorer are either deposited farther down, or are carried by the force of the stream into the canal, F, F', by which they are conducted into other basins where they are allowed to settle. When the table has become covered with a certain quantity of matter, the workman prevents the arrival of any fresh ore at the top of the platform, and begins to sweep by means of a small broom the mineral from the lower end of the inclined plane towards the higher. This operation is commenced at the point q; and, as a stream of pure water is now allowed to flow over the table, a still further purification is thus effected, since the poorer particles which may have become accidentally entangled with the heavier portions are thus eliminated.

When the mineral is considered sufficiently pure, a value is opened at the point g; and the contents of the table are swept through the opening into hutches placed beneath for their reception. The value is then closed, and the operation repeated on another portion of ore, which, like the former, is finally conducted into boxes placed for that purpose beneath the tables, and from whence it may in most instances be conveyed directly to the smelting house. The inclination given to tables of this kind is regulated by the nature of the work to be treated. If this be extremely fine, the inclination is small, but if it be in the form of a coarse powder, the planes on which it is washed are made to take a more decided dip.

The Percussion Table, fig. 78, consists of a wooden flooring, A, B, nailed on strong wooden sleepers for the purpose of imparting to



78.

it a considerable degree of weight and solidity. This is suspended by four chains or articulated iron rods, a b, a' b', c d, c' d': of these the two former, a b, a' b', are fixed to an immoveable wooden framework, whilst the two latter are attached to a long forked lever, c, c, moving on the centres e, e', and capable of being raised or depressed by a pin placed in the holes of the upright f, f'. This arrangement affords the means of varying the inclination of the table, A, B, and consequently of adapting it for washing ores of different degrees of fineness.

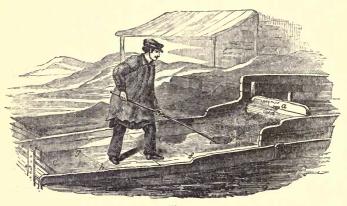
The axle D D' set in motion by a water-wheel, is provided with cams: g g' g'' acting on the wooden lever E, connected with the swinging-table A B, which it first pushes back, and then allows to fall with considerable force against two wooden stops arranged for that purpose.

At the head of the suspended platform A B, is placed a triangular shelf, F, similar to that employed in the sloping table just described, and like them provided with triangular pieces of wood for spreading the water uniformly over its surface.

The mineral to be washed is placed in the trough, G, where it becomes mixed with water arriving through the spout n n'. It

then passes on to the platform, F, at the head of the table, and afterwards to the suspended plane itself, where it will have a tendency to arrange itself according to its specific gravity, and settle as a thin deposit over the surface. The constant shocks to which this arrangement is exposed has, however, the effect of again suspending the particles in water, so that each atom of which the deposit consists has repeated opportunities of placing itself in the position corresponding to its size and density, and consequently of being separated from the lighter earthy impurities. These tables are employed for washing the same kinds of minerals as the sleeping tables, the one or the other being preferred according to the nature of the gangue from which the ore has to be separated. The inclination given to the table will depend on the degree of fineness to which the ore has been reduced, as will also the frequency and force of the blows, and the quantity of water to be employed.

In the mines of Cornwall neither of these contrivances are employed, and the concentration of the bruised ore is chiefly effected by the use of *buddles* and *racks*.



79.

The Nicking-Buddle, fig. 79, consists of a long cistern with an inclined floor, very similar in appearance to a German chest, although the methods of working the two are extremely different.

At the head, A, of the buddle is a rectangular head-board, similar to those of the arrangements last described, except that it is not provided with water-guides, as are the platforms of the sleeping and percussion tables of the Continent. At a, a current of water, regulated by a wooden plug, is brought on the inclined upper shelf, and on this the mineral to be washed is placed. This is done by a boy who takes care to reduce all the lumps it may contain before placing it in the water, whilst another boy, who is generally older than the first, and consequently has more experience of the work, stands in the pit itself, and with a sharp-pointed shovel alternately smooths and notches the charge on the headboard. The notches made on the ore are rapidly effected by the shovel in the direction of the current of water, and at the next instant all obliterated, to give place to a quick succession of others, which are made in their turn to disappear. The ore is thus speedily washed from the head, A, into the buddle itself, B C, when the boy, instead of immediately adding a fresh supply on the triangular head, commences to brush the layer which has formed in the direction of c to B, which smooths its surface, and not only prevents its being spread unevenly by the water flowing over it, but also, by disturbing the particles of which it is composed, causes them to arrange themselves more perfectly in accordance with their different densities. The effect thus produced by sweeping with a broom is somewhat similar to that obtained by the repeated shocks of the percussion table, and the lighter portions, which are held in suspension in water, are carried off through the holes, c, into pits prepared for their reception. When the deposit of the heavier particles has reached the level of the lowest hole, and they consequently begin to escape, the aperture is stopped with a plug, and the water and suspended gangue allowed to flow out of that which is next above it in the series. As soon as the level of the deposit has reached this point, it is in its turn plugged, and so on, until the pit, B C, is entirely filled. When this is the case, the sand is consolidated by making a series of long cuts with the shovel in the direction of its length, and, when sufficiently drained, the contents are divided into three classes, as shown by the lines e f, g h. Of these, that which is nearest to the head of the pit is necessarily the richest in ore, and is frequently sufficiently pure for the purposes of the smelter. The second division is usually laid aside to be again buddled, whilst the third portion, which consists of the finer and poorer particles, is treated on the rack-frame, now to be described.

The Rack, fig. 80, consists of a smooth wooden flooring, F, nailed on the under side of a strong framing, g g, suspended in a slightly inclined position by the pivots, P r', and having a headboard similar to that of the buddle. In order to admit of turning the table on its axes, it is not attached to the head, H, but the water is carried from the higher to the lower level, by a flap, v, hung on leather hinges, and which admits of being easily raised, when the rack itself is made to move on its pivots. To use this table the ore to be washed is placed on H, and a stream of water admitted through an aperture, partially stopped



by a wooden plug. The pounded mineral is then alternately furrowed and flattened, as in the case of the buddle; but instead of this being done by a shovel, a wooden hoe is used for that purpose. After two or three successive charges have in this way been transferred from the upper ledge to the lower table, **F**, which has a slight inclination, the deposit is moved by the wooden rake towards the most elevated part of the floor, a sheet of clean water being at the same time conducted over its surface. By this treatment, and successive washings with a small heath-broom, the particles of ore are ultimately separated from the lighter earthy impurities, which are carried by the water to the bottom of the rack, where they escape through the opening into reservoirs prepared for their reception.

When a sufficient layer of mineral has by this manipulation been collected on the table, it is made to take a quarter revolution on its axes, and, when in a vertical position, is caught by a wooden spring, which holds it firmly in that situation.

The person working the frame now washes off the ore by the use of a wooden bowl with a long handle, which causes it to fall first into the angle formed by the meeting of the side, g, and the floor,  $\mathbf{r}$ , and ultimately into boxes placed beneath for its reception. In this, as in the preceding examples, the richer ore will be found to accumulate at the upper end of the inclined plane, and therefore

the washed ore is divided into two parts, each of which falls into a different receptacle.

This division is made by a fillet, placed on the side of the rack at about equal distances from its two extremities, and which, when the plane is brought in a proper position for washing off the deposited metalliferous grains, forms a dam, and causes that which is deposited on the upper part of the floor to fall into one box, or *cover*, whilst that which is deposited on the lower falls into another.

Many other methods are employed in various parts of the world for washing different kinds of ores, but in all cases the purification depends on similar principles, and the processes are only varied to suit some peculiarity of the minerals operated on. The mechanical preparation of mineral substances is, however, a very tedious and delicate operation, and one that requires considerable skill and experience, as a process which may perfectly succeed with an ore and in one locality, will not be found to yield satisfactory results in another situation, as the nature of the gangue with which it is associated, and its state of aggregation, will be found to materially influence the results obtained.

# FUEL.

WITH but few exceptions the operations employed for the extraction of the metals from their ores require the aid of very elevated temperatures, and consequently it is important that the metallurgist should be fully acquainted with the different properties of the various kinds of fuels, and be thereby enabled to judge under what circumstances they may each be most economically employed.

**Wood.**—The roots, trunks, and branches of trees are called wood. Ordinary wood consists of three distinct portions,—woody fibre (composed of carbon, hydrogen, and oxygen), the constituents of the sap and water. Recently felled timber contains all three of these ingredients, but loses a large proportion of its water by exposure to the air. The relative proportion of these ingredients differs in the various kinds of woods, and is also considerably affected by the seasons of the year at which the different specimens are felled. When trees are cut during the winter months, and therefore not in a state of active vegetation, this proportion is found to be less than if felled in the summer when full of sap; and consequently all wood should (unless prevented from some special cause) be felled during the colder portion of the year.

Some kinds of trees are cultivated, not only for the timber which they yield, but also on account of the tannin contained in their barks; and such species are usually cut during the flow of the sap, as they are at that time more easily barked, and likewise contain a larger proportion of the compound, on account of which their bark is collected.

The small shoots and twigs yield a larger per centage of water than the more solid stem, and this difference is also very considerable in many woods of a like nature, but of different botanical species, as may be observed by inspection of the following numbers, given by Schübler and Hartig.

100 parts of fresh cut wood from the

WATER.	WATER.
Hornbeam (Carp. betul.) contain 18.6	Wild service tree (Crataeg. tormi-
Willow (Sal. caprea) 26.0	nalis)
Sycamore (Ac. pseudoplat.) 27.0	Oak (Querc. robur)
Mountain ash (Sorb. ancupar.) . 28.3	Pedicle Oak (Q. pedunculata) . 35.4
Ash (Fraxin excelsior) 28.7	White Fir (Pin. Abies dur) 37.1
Birch (Betula alba)	Horse-chesnut (Aescul. hippocast.)38.2

WATER.	WATER.
Pine (P. sylvester L.) contain . 39.7	Lime tree (Tilia europæa) • 47.1
Red Beech (Fagus sylvat.) 39.7	Italian Poplar (Pop. dilatat.) . 48.2
Alder (Betul. alnus) 41.6	Larch (Pin. larix) 48.6
Asp (Popul. tremula) 43.7	White Poplar (Pop. alba) 50.6
Elm (Ulmus campestr.) 44.5	Black Poplar (Pop. nigra) 51.8
Red Fir (P. picea. dur) 45.2	

It therefore follows that recently cut wood contains from onefifth to one-half its weight of water, which would not only detract from its value as a fuel, in the same proportion, but, from its escaping in the form of vapour, must, moreover, carry off a part of the heat developed by the combustion of the other elements.

By exposure to the air green wood soon loses a portion of its water, but after a time it ceases to diminish in weight, as a sort of equilibrium is established between the hygroscopic power of the air and that of the wood itself. When this occurs no further drying is effected by continued exposure, and its per centage of water will only vary within very narrow limits, dependent on the dryness or humidity of the situation in which it is placed.

In this state wood is said to be *air-dried*, and the remaining portions can only be expelled by the aid of heat, the last traces being eliminated with extreme difficulty.

Count Rumford, who heated specimens of various kinds of airdried woods at a temperature of 277° Faht. until they ceased to lose weight, obtained the following results :---

	pa		

Oak wood lost	.0	16.64	Fir wood lost 1	7.53
Elm		18.20	Birch 1	9.38
Beech		18.56	Lime 1	8.79
Maple		18.63	Poplar 1	9.55

Generally speaking, however, the wood employed for fuel is never thoroughly dried, but retains from 20 to 25 per cent. of water, so that the driest specimens seldom contain more than 80 per cent. of combustible matter. Wood several years old, kept in a warm room for six months, still retains, according to Winkler, 17 per cent. of water. Woods are usually divided into two classes —hard and soft. This distinction is founded on the calorific properties and the facility with which they can be worked by edge-tools.

The former, among which are numbered oak, beech, white and red birch, elm, and alder, contain in the same bulk a larger proportion of fibre, and have their vessels more closely packed than those of the softer varieties,—such as pine fir, white fir, larch, lime, willow, and the various kinds of poplar.

Trees which have grown in poor land and in exposed situations, are found to produce harder and denser wood, than others of the same kind, which have been planted in more sheltered localities and richer soils. The specific gravity of wood depends in a great measure on its structure; but as two specimens of the same tree can never be found perfectly homogeneous, the results obtained by experiment should rather be considered as approximative than as representing the true density of the wood examined. These variations of specific gravity will also be influenced, to a certain degree, by the nature of the soil in which the tree has grown, as on this will depend in a great measure the quantity and character of the salts which it contains.

From the air contained in their cavities, woods are in their ordinary state generally lighter than the same bulk of distilled water; but when reduced, by rasping, to the state of fine powder, even the softest varieties are found to possess a greater density than that liquid. By thus destroying the pores, and liberating the enclosed air, the specific gravity of the following woods was found to be—

Oak					1.27	Fir .		•		1.16
Lime	•	•	•	•	1.13	Fir . Beech		•	•	1.29

In the following table the respective densities of the different kinds of wood in their various states are given according to the best authorities :—

Variety of Wood.		1. Recently Felled.	2. Dried in Air.	3. Strongly Dried.
Common Oak (Quercus robur) .		1.0754	0.7075	0.663
Pedicle Oak (Q. pedunculata) .	.	1.0494	0.6777	0.663
White Willow (Salix alba).	.	0.9859	0.4873	0.457
Beech (Fagus sylvatica) .		0.9822	0.5907	0.560
Elm (Ulmus campestris)	.	0.9476	0.5474	0.518
Hornbeam (Carpinus betulus) .	.	0.9452	0.7695	0.691
Larch (Pinus larix)		0.9205	0.4735	0.441
Scotch Fir (Pinus sylvestris) .		0.9121	0.5502	0.485
Sycamore (Acer pseudoplatanus).	.	0.9036	0.6592	0.618
Ash (Fraxinus excelsior)		0.9036	0.6440	0.619
Birch (Betula alba)	.	0.9012	0.6274	0.598
Mountain Ash (Sorb. ancuparia).	.	0.8993	0-6440	0.552
Fir (Pinus abies, Duroi)		0.8941	0.5550	0.493
Silver Fir (Pinus picea, D.)		0.8699	0.4716	0.434
Wild Service (Crat. torminalis) .		0.8633	0.5910	0.549
Horse-chesnut (Aesculus hippoc.).		0.8614	0.5749	
Alder (Betula alnus)		0.8571	0.5001	0.443
Lime (Tilia Europæa)		0.8170	0.4390	0.431
Black Poplar (Populus nigra) .		0.7795	0.3656	0.346
Aspen (Populus tremula)		0.7654	0.4302	0.418
Italian poplar (Populus italica) .		0.7634	0.3931	
Ebony	.		1.2260	-

Specific Gravity of different kinds of Wood.

The columns 1 and 2 give the densities determined by Hartig, and column 3 the results obtained by Winkler, who weighed a cubic inch of each kind of wood.

Wood not only loses weight by exposure to air, but at the same time decreases in bulk; and in some varieties this takes place to the extent of one-tenth of its original volume.

By long immersion in water, the soluble and extractive matter contained in woods is dissolved, and therefore the method of transporting it by rafts, as practised in some countries, is not only found to lessen its weight, but also to reduce its calorific powers; and consequently the advantages of cheap transport are in part counterbalanced by the inferiority of the wood thus conveyed.

The proximate analysis of different kinds of wood yields results little differing from each other; but in all the varieties which have yet been examined there is a slight excess of hydrogen over the oxygen, although, in pure woody fibre, they are combined in such proportion as, by their union, to form water. The results of Schödler and Petersen are given in the following table. The different kinds of wood were, in these experiments, first reduced to the state of powder, and then dried at 212° Fah. until they ceased to lose weight.

Species of Wood.	Carbon.	Hydrogen.	Oxygen.
Pure woody fibre	52.65	5.25	42.10
Quercus robur	49.43	6.07	44.50
Fraxin. excelsior	49.36	6.07	44.57
Acer campestris	49.80	6.37	43.89
Fagus sylvatica	48.53	6.30	45.17
Betula alba	48.60	6.37	45.02
Ulmus campestris	50.19	6.42	43.39
Populus nigra	49.70	6.31	43.99
Tilia Europæa	49.41	6.86	43.73
Salix fragilis	48.44	6.36	44.80
Pinus abies	49.95	6.41	43.65
Pinus picea	49.59	6.38	44.02
Pinus sylvestris	49.94	6.25	43.81
Pinus larix	50.11	6.31	43.58

100 Parts yielded :---

The nature and amount of the ashes left by the combustion of the various kinds of wood, depends, not only on the species of tree examined, but is also, to a certain degree, influenced by the nature of the soil on which it has been produced, as the different

#### FUEL.

inorganic substances which enter into the composition of organic bodies, seem to have, to a great extent, the power of replacing each other in the same way that one isomorphous substance may be substituted for another without affecting the form of a crystalline body. Generally speaking, the ashes of wood contain, besides potash or soda, or both, lime, magnesia, and iron, combined with carbonic, silicic, sulphuric, and phosphoric acids, together with the chlorides of their radicals.

Fir	0.0083	Elder Tree	0.0164
Birch	0.0100	Arbre de Judée .	0.0170
False Ebony	0.0125		
Hazel			0.0600
White Mulberry .	0.0160	Lime Tree	0.0200
Saint Lucia	0.0160		

The different parts of the same tree do not yield equal proportions of incombustible matter; the bark and leaves always produce a larger amount than the branches, whilst the branches leave more than the trunk. Woody plants generally yield less than herbaceous ones, which are also remarkable for containing a larger proportion of silica than is usually met with in wood ashes.

The experiments of Berthier on the ashes of various kinds of trees afforded him the following results :---

효 Carbonic Acid Sulphuric Acid	Oak.	Lime Tree.	18.8	Fir. 30·2	Mulberry.
	$5.9 \\ 4.0$	$7.6 \\ 1.8$	$8.7 \\ 0.5$	$3.1 \\ 0.3$	8·3 4·0
[马] Silica	1.0	1.7	2.7	1.0	
$\begin{bmatrix} Potash \\ Soda \end{bmatrix}$	<b>60.7</b>	60.7	69.3	65.4	52.0 11.5
	100.0	100.0	100.0	100.0	98.8

Table showing the Composition of the Ashes of various Trees.

<sup>1</sup> Berthier, Essai par la Voie Seche, Vol. i. p. 259.

<sup>2</sup> According to the theory at present received among chemists, hydrochloric acid does not combine directly with the alkalies, but chlorine becomes united to the metallic radical, water at the same time being formed. In the above table the author's results are given in his own words.

	in monadus.	Oak.	Lime Tree.	Chesnut.	Fir.	Mulberry.
	Carbonic Acid .	30 1	39.8	30.5	23.0	42.0 .
ter	Phosphoric Acid .	7.0	2.8	1.9	4.2	1.8
Iat	Silica	1.7	2.0	8.5	8.0	2.9
Insoluble Matter.	Lime	44.7	51.8	51.1	39.8	46.1
pla	Magnesia	7.9	2.2	3.8	4.4	4.6
lu	Oxide of Iron .	0.1	0.1	3.5	14.1	0.5
nse	Oxide of Manganese	2.9	0.9	1. 1. 1. 1. 1.	6.0	1.3
I	Charcoal, &c	4.5	100	-		
-11	and the second	98.8	99.3	99.3	99.5	99.2

Turf and Peat.-In low and moist situations, where water collects and cannot easily flow off, and in which the loss by evaporation is inconsiderable, large swamps or moors are formed, and in these, water-plants of all kinds, such as sedges, rushes, reeds, mosses, algæ, and even small shrubs, grow with great rapidity, and quickly cover the surface with a thick layer of vegetation. As winter comes on, these die and fall to the ground, and are, on the return of spring, themselves covered with another crop of similar plants. These changes go on from year to year, and finally the bottom of the valley becomes covered with a thick layer of vegetable matter in a very loose state of aggregation. After a time, decomposition takes place in the mass, carbonic acid and marsh gas (light carburetted hydrogen), together with small quantities of sulphuretted hydrogen, are evolved, produced by the reduction of the sulphates present, and finally the whole attains a considerable density and becomes of a dark earthy colour.

This substance is called *peat*, and is in many places extensively employed for the purpose of producing heat. There are but few localities in which small quantities of this substance are not found; but in some countries, such as Holland and North Germany, such formations extend over districts of immense extent, and annually furnish large amounts of fuel to the various manufactories in their vicinity.

Sometimes the different deposits of peat appear to have taken place at successive periods, and in this case they are generally divided into parallel horizontal strata by layers of sand of various thicknesses. The layers nearest the surface are for the most part less compact, and of a lighter colour, than those found deeper in the series, and are made up of the roots and stems of plants, which although more or less decomposed, still retain their original forms

This porous spongy substance is called *turf*, and generally becomes of a darker colour and greater density as its depth

increases; finally, it loses all outward traces of its vegetable origin, and is transformed into a dark muddy substance called *peat.* 

Peat consists of turf so far decomposed that no traces of its original organic structure remain, and of which the fracture has become compact, and in some instances even resinous. Its density is also always greater than that of the more recent variety, of which a cubic foot, on an average, only weighs from four to six pounds, whilst the weight of the same bulk of ordinary peat varies from twelve to twenty pounds.

The cutting of peat is a very simple operation. After having laid bare the surface, the peat is cut by square-pointed shovels in the shape of rectangular blocks, which are afterwards dried in the sun, and subsequently stacked, either to be employed for metallurgical purposes, or to be used for ordinary fires. In some instances the surface of the ground is covered with water, which, from want of level, cannot be drawn off; and in such cases the peat is collected by means of an instrument called a louchet. This consists of a square-pointed shovel provided with an edge turned up at right angles for the purpose of affording a hold for the block after its separation from the mass. To use this tool, a man stands on a stage raised a little above the surface of the water, and, having thrust the instrument into the peat, withdraws it, together with a small cube of the combustible, attached by its adhesion to its two sides. When the depth of the water is more considerable, a larger instrument is employed, which is worked by two men, and provided with a spring for holding the detached cube of peat with sufficient firmness to allow of its being drawn to the surface, where the spring is released and the charge withdrawn.

In Holland, when the peat has become too spongy to be further extracted by the method above described, and is reduced to the state of black mud, it is obtained by the use of a sort of dredge, made of a sharp steel hoop, to which is attached a bag of close network, which allows the water to flow through, but retains the particles of peaty matter scraped from below the surface of the water. These are allowed to drain in wooden troughs of which the bottoms are covered with straw, and in which numerous holes are bored for the purpose of allowing the water to escape. When the mass has thus attained a certain consistence, it is trodden down by persons wearing large pieces of wood, like snow-shoes, on their feet, to prevent their sinking into it, and when sufficiently firm to resist the pressure of the foot, it is beaten with a peculiar kind of beater until nearly all the water is expelled. It is now cut into blocks not unlike bricks, and stacked

under proper sheds, so as to allow currents of air to pass between the different layers and thereby facilitate the drying of the blocks.

The ashes which remain after burning peat are partially derived from the salts originally contained in the vegetables of which it is composed; but by far the largest proportion arises from earthy matters subsequently deposited from the water which so frequently covers the surface of the moors in which it is produced.

The composition of the ashes of peat will necessarily be influenced to a great extent by the nature of the soil in the neighbourhood where it is formed, as the water descending from higher grounds during heavy rains will always carry with it, in suspension, small particles of the earth of which they are composed, and which is deposited in the form of sand on reaching the lower lands, where it accumulates. In fact, it is constantly observed that the ashes of peat from a calcareous district will principally consist of carbonate of lime, whilst a specimen which has been formed amongst hills of igneous origin yields an ash in which siliceous sand predominates.

In 100 parts of peat the following quantities of ash have been observed :----

Variety of Peat.	Ash.	Observers.
Grass Peat, brownish yellow	17.30	1
Pitch Peat, from Clermont	26.00	Berthier.
Herbaceous, from Burgundy	7.10	> Dertmer.
Brown and Herbaceous, from Troyes	16.00	and the second
Very old Peat, from Vulcaire, near Abbeville .	5.88	j and a call
" Long	4.61	- Regnault.
Not so old, from Champ de Feu	5.35	)
Near Berlin, 1st stage	9.30	5
" " 2d "	10.20	Achard.
" " 3d "	11.20	
Moor in Eichsfeld, 1st sort	21.50	1
" " 2d "	23.00	Buchholz.
" " 3d "	30.50	buchholz.
" " 4th "	33.00	
Yellowish brown, from Dartmoor	13.43	J. A. Phillips.
a preside all reliable formate with the second party		KITS LABORA

After deducting the ash, Regnault obtained the following per-centage amounts from three specimens of peat, included in the foregoing table:—

	Carbon.	Hydrogen.	Oxygen and Nitrogen.
Peat from Vulcaire	57.03 .	. 5.63 .	. 31.76
" Long	. 58.09 .	. 0.93 .	. 31.37
" Champ de Fe	u 57.79 .	. 6.11 .	. 30.77

K

# COAL.

Fossil fuel is found in three distinct formations-

1stly. In the *tertiary formation*: fresh water limestone, shell limestone, &c.

2ndly. In the secondary formation: both in the older Keuper and Jura formations, and in the more recent chalk.

3rdly. In the *coal formation*, which is subdivided into the older *transition formation*, producing anthracite; and the newer *coal formation*, yielding coal.

Lignite, or Brown Coal, from the tertiary formation, varies very much in its appearance and composition, and has consequently received from mineralogists several distinct names, such as *brown* coal, bituminous wood, common lignite, and earthy lignite. Of these, the former very much resembles turf in its nature, consisting of woody matter, which in many instances so far retains its original structure as to admit of the recognition of the class to which the tree belonged. This kind frequently loses about 20 per cent. of water at a heat of 212° Fah., and yields from 35 to 40 per cent. of a brittle coke resembling charcoal.

The second variety, or bituminous wood, although it still presents to a certain degree its woody texture, is generally of a very dark brown or black colour, and more closely resembles in its nature some varieties of mineral pitch than the wood from which it was originally formed.

At Meiszner, in Germany, a deposit of bituminous wood is covered by a stratum of basalt more than three hundred feet in thickness, and occurs in flattened fragments which still retain the laminated structure of wood. Its transverse fracture is conchoidal and glossy, its specific gravity 1.32, and the usual colour of the substance, either dark brown or black. When burnt, it decrepitates on the fire, giving off a very disagreeable odour, and leaves about 14 per cent. of ash.

Common lignite very much resembles in its appearance coals from the secondary formations. Its usual colour is black or brown, with a compact structure and irregular fracture. Sometimes the fracture is conchoidal and brilliant, and in this case the substance is often called *jet*, although the true jet from which ornaments are manufactured is not a variety of lignite. This substance contains a less proportion of water than the variety known by the name of fossil wood, and has an average specific gravity of 1.20. When heated, it gives off inflammable gases, together with acid and tarry matters; but the resulting coke in most instances retains the form of the fragment from which it was

#### LIGNITE.

produced. Less frequently, the lignites may be so far softened by heat as to run together and cake on the fire, or even to assume a tarry consistence; but these specimens are only to be obtained from deposits occurring in the fresh-water limestone formations.

The earthy lignites, as their name implies, contain a large proportion of incombustible foreign matter. They have a dark brown colour and hackly fracture, and, from the quantities of iron pyrites and clay which they contain, are sometimes burnt for the purpose of manufacturing alum and copperas from the ashes they thus afford.

The following table shows the per-centage composition of several varieties of lignite :---

Variety of Lignite.	Ash.	Carbon.	Hydrogen.	Oxygen, Sulphur, & Nitrogen.	Observers.
Earthy, from Dax.	4.99	70.49	5.59	18.93	1.
Bouches du					
Rhône	13.43	63.88	4.58	18.11	} Regnault.
Nieder-Alpen .	3.01	70.02	5.20	21.77	Participation ( Jam)
Meiszner	19.10	70.12	3.19	7.59	1 Contractor
Pitch Coal	11.50	56.60	4.75	27.15	
Ringkuhl	10.17	60.83	4.36	24.64	} Kühnert.
Cannel Coal from				The second second	11111111111111111111111111111111111111
Ringkuhl	10.56	66.11	4.82	18.51	Justing a set
Wigan	4.95	80.21	6.30	8.54	J. A. Phillips.
Conception Bay Lignite, from Sandy	7.49	70.33	5.84	16.34	Admiralty
Bay, Patagonia	13.29	62.19	5.08	19.44	Coals Investi-
Talcahnano Bay	6.92	70.71	6.44	16.93	gation.
Ringkuhl	12.68	51.70	5.25	30.37	Kühnert.
Greece	9.01	61.21	5.00	24.78	
Cologne	5.49	63.29	4.98	26.24	Regnault.
Usnach	2.19	56.04	5.70 .	36.07	
Laubach	0.49	57.28	6.03	36.10	Summer and the

The specific gravity of the different varieties of brown coal varies, but within narrow limits. Regnault found the specimens of lignite which he examined to possess densities of from 1.10, to 1.85. The earthy lignites analysed by Kühnert weighed from 1.310 to 1.436, whilst the several varieties tested by the officers of the "Admiralty Coals Investigation" had specific gravities varying from 1.291 to 1.321: hence the weight of a cubic foot of lignite will, on an average, be about 75 pounds. Of Mineral or Pit Conl.—This substance is found in seams of varying thickness in the carboniferous and secondary formations, but occurs in much larger quantities than any of the beforementioned varieties of fuel.

Although at the present day of such vast importance to the manufacturing industry of this and other countries, its employment as fuel is of comparatively recent date. Its valuable properties appear to have been first discovered by the Chinese, who, according to the testimony of Marco Polo, have from remote antiguity been acquainted with a "black stone, which, when thrown on the fire, burns like wood." In Europe, the employment of this combustible arose from the gradual decrease in the supply of wood, and in the year 1238 the first colliery was opened on the high grounds in the neighbourhood of Newcastle-on-Tyne. This was followed in 1330 by another mine near Lanchester, and in 1500 by those of Gateshead, Wickham, Tynemouth, and many Since this period the great advances made in every others. department of the industrial arts, and the application of steam as a motive power, have caused a rapidly increasing demand for fuel, which has led to a diligent search for this valuable substance in almost every part of the civilised world. In England the principal coal districts are Northumberland, Durham, Yorkshire, Cumberland, Staffordshire, Lancashire, and Cheshire. There is also an abundance of this fuel found in many parts of Scotland, in North and South Wales, and in some parts of Ireland. the continent of Europe, the supply is comparatively much less abundant than in England, although considerable quantities are annually obtained from the mines of central France, Belgium, Westphalia, and Upper and Lower Silesia. Large deposits of fossil fuel also occur in the United States of America, in Borneo, and on the Australian continent.

Veins of coal are worked by means of shafts and galleries in the same way that metallic minerals are extracted from the lodes in which they are found; but as the seams of coal are generally much more extensive than the metallic deposits, and much larger masses are consequently removed from the interior of the mines, the greatest care is required, not only to prevent the crushing together of the workings, but also to induce a current of air into every part of the colliery in such a way as to furnish the workmen with fresh air for the purposes of respiration, and prevent the accumulation of the explosive gases which frequently issue from beds of coal. The great number of varieties of coal has given rise to distinctions founded partly on its age and appearance, and partly on its quality.

In all kinds of coal the structure of the wood from which they

have been formed is obliterated, although partial impressions of plants indicating their origin frequently occur. Coals generally form a more or less compact mass of a dark brown or black colour, sometimes dull, but more frequently possessing a vitreous lustre, which often exhibits a decided iridescence. Their specific gravity is considerably above that of wood, and their structure decidedly granular. They are always distinctly stratified, and have generally a cleavage at right angles to the plane of deposition. The different laminæ of which they are made up are usually in close contact with each other, but are sometimes found to be separated by thin layers of other minerals, such as iron pyrites, carbonate and sulphate of lime, galena, sulphate of baryta, the soda salts, and still more frequently by a double carbonate of lime and iron.

The fracture of the shining kinds of coal is conchoidal, and that of the duller varieties hackly. Common coal, and particularly that from the newer formations, is observed to be made up of layers of very different appearance: the one kind, which is black and shining, and has a conchoidal fracture, is rich in carbon; whilst the duller variety, which is of a brown colour, contains a smaller amount of that element, and has a soft velvety structure.

When coal is compact, and has a resinous lustre, it is called *pitch coal*; that which has a cubical fracture is called *cubical coal*; if it agglomerates by heat, and partially melts on the fire, it is named *caking coal*; and when it can be easily split into thin leaves parallel to the lines of deposition, it is known by the name of *slate* or *splint coal*. On extracting coals from the pit, and leaving them exposed to a dry atmosphere, they lose a portion of the moisture with which they are more or less saturated on leaving the mine, but still retain a certain amount, varying from 1 to 12 per cent., according to their mechanical structure. The following table, extracted from the Third Official Report on the Coals suited to the Steam Navy, shows the per-centage composition of several varieties of British coals, together with their specific gravities, and the amount of ash and coke yielded by each. (See Table, page 134-135.)

The results obtained by Regnault and Karsten from several varieties of foreign coals, are given in page 136.

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Per-centage of Coke left by each Coal.	85.0 77.5 86.53 88.10 88.10 88.25 88.83 88.583 88.583 88.54 83.9	$\begin{array}{c} 72.19\\ 65.13\\ 65.13\\ 69.69\\ 64.61\\ 64.61\\ 72.81\\ 72.81\\ 59.20\\ 35.60\end{array}$
Ash.	$\begin{array}{c} 1\cdot45\\ 1\cdot50\\ 1\cdot50\\ 3\cdot26\\ 3\cdot26\\ 5\cdot94\\ 5\cdot34\\ 5\cdot34\\ 0\cdot41\\ 0\cdot41\end{array}$	$\begin{array}{c} 1 \cdot 0 \\ 2 \cdot 1 \cdot 0 \\ 2 \cdot 1 \cdot 1 \\ 2 \cdot 1 \cdot 2 \\ 2 \cdot 5 \cdot 1 \\ 2 \cdot 0 \\ 4 \end{array}$
Oxygen.	0.94 0.39 0.39 0.60 0.60 2.53 1.03 1.50 3.82 1.65 3.82 1.65 1.65 1.65 1.65 1.82 1.85 1.82 1.85 1.85 1.85 1.85 1.85 1.85 1.85 1.85	$\begin{array}{c} 5\cdot 2\\ 5\cdot 2\\ 6\cdot 6\\ 6\cdot 6\\ 2\cdot 2\\ 2\cdot 5\\ 6\cdot 5\\ 1\\ 7\cdot 5\\ 6\cdot 4\\ 6\cdot 4\\ 6\cdot 4\end{array}$
Sulphur.	$\begin{array}{c} 1\cdot18\\ 1\cdot02\\ 0\cdot85\\ 1\cdot77\\ 1\cdot77\\ 1\cdot27\\ 1\cdot27\\ 1\cdot27\\ 1\cdot27\\ 0\cdot33\\ 3\cdot50\\ 0\cdot34\\ 0\cdot34\\ 0\cdot91\\ 0\cdot84\\ 0\cdot87\\ 0\cdot87\\$	$\begin{array}{c} 0.88\\ 1.32\\ 0.65\\ 1.32\\ 1.69\\ 1.78\\ 1.135\\ 1.35$
Nitrogen.	$\begin{array}{c} 1.2\\ 2.16\\ 1.2\\ 1.45\\ 1.45\\ 1.45\\ 1.45\\ 1.46\\ 1.46\\ 1.06\\ 1.09\\ 1.38\\ 1.38\end{array}$	$\begin{array}{c} 1\cdot 0.5\\ 1\cdot 26\\ 1\cdot 26\\ 1\cdot 26\\ 1\cdot 28\\ 1\cdot 28\\ 1\cdot 52\\ 1\cdot 69\\ 1\cdot 69\\ 1\cdot 61\\ 1\cdot 61\end{array}$
Hydrogen.	$\begin{array}{c} 4.28\\ 5.15\\ 5.15\\ 4.66\\ 4.66\\ 6.01\\ 4.53\\ 4.53\\ 4.53\\ 4.51\\ 4.51\\ 4.51\\ 4.51\end{array}$	$\begin{array}{c} 4.96\\ 5.31\\ 5.32\\ 5.28\\ 5.28\\ 5.28\\ 5.26\\ 5.424$ 5.424\\ 5.424 5.424\\ 5.424 5.424\\ 5.424 5.424 5.4222\\ 5.424 5.4222 5.4222 5.4222 5.4222 5.4222 5.422 5.422 5.422 5.422 5.422 5.422 5.4
Carbon.	$\begin{array}{c} 990.94\\ 990.78\\ 882.26\\ 982.26\\ 982.26\\ 882.49\\$	$\begin{array}{c} 86\cdot81\\ 85\cdot58\\ 85\cdot58\\ 82\cdot47\\ 83\cdot47\\ 81\cdot81\\ 81\cdot81\\ 81\cdot81\\ 81\cdot81\\ 81\cdot85\\ 80\cdot26\\ 81\cdot85\\ 80\cdot75\\ 82\cdot24\\ 82\cdot25\\ 82\cdot24\\ 82\cdot25\\ 82\cdot24\\ 82\cdot25\\ 82\cdot24\\ 82\cdot25\\ 82\cdot25\\ 82\cdot24\\ 82\cdot25\\ 82\cdot24\\ 82\cdot25\\ 82\cdot24\\ 82\cdot25\\ 82\cdot25\\ 82\cdot24\\ 82\cdot25\\ 82\cdot24\\ 82\cdot25\\ 82\cdot24\\ 82\cdot25\\ 82\cdot25\\ 82\cdot24\\ 82\cdot25\\ 82$
Specific Gravity of Coals,	$\begin{array}{c} 1\cdot305\\ 1\cdot275\\ 1\cdot275\\ 1\cdot275\\ 1\cdot304\\ 1\cdot304\\ 1\cdot304\\ 1\cdot32\\ 1\cdot32$	$\begin{array}{c} 1\cdot26\\ 1\cdot26\\ 1\cdot28\\ 1\cdot28\\ 1\cdot21\\ 1\cdot25\\ 1\cdot25\\ 1\cdot23\\ 1\cdot23\\ 1\cdot23\end{array}$
Locality or Name of Coal.	We have a series of the second	Kerrich Martews House, Tanfield Andrews House, Tanfield Bowden Close Newcastel Hartley Fieldey's Hartley Bates' West Hartley West Hartley Main Buddle's West Hartley Hastings' Hartley

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FUEL.

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Coals-continued.
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TABLE

Per-centage of Coke left by each Coal.	61-6 62-5 61-7 61-7 60-9 54-9 57-86 52-8	64-0 58-1 62-89 67-84 60-6 55-7	58.45 59.15 53.5 53.6 53.6 52.03 54.94 54.94 54.94
Ash.	2.46 3.73 3.73 1.23 4.65 2.40 2.40 2.30	1.53 3.42 3.32 4.05 2.34 6.58 6.58	10-70 2-89 3-10 1-25 4-00 3-52 2-44 4-87 4-87
Oxygen.	8.58 8.99 9.95 11.26 9.86 10.96 12.41	7.44 10.65 5.28 7.53 10.91 7.98	5.05 6.37 14.37 11.31 8.33 8.58 8.58 8.05 15.51
Sulphur.	0.91 1.06 1.11 0.86 1.14 0.72 1.30	0.80 0.52 1.05 1.43 1.43 1.73 3.04	1.53 1.57 0.38 0.86 0.86 1.46 1.42 1.38 0.33
Nitrogen.	1-27 1-24 2-15 2-15 0-80 1-23 1-64	$\begin{array}{c} 1.76 \\ 0.54 \\ 0.98 \\ 1.68 \\ 1.68 \\ 1.80 \\ 0.50 \\ 2.05 \end{array}$	1.41 1.53 1.53 trace 0.94 1.13 1.65 0.10
Hydrogen.	4 85 4 93 5 65 4 86 5 88 4 88 8 4 8 8 4 86	5.86 5.24 5.52 6.53 6.53 7.65 7.65 7.65 7.65 7.65 7.65 7.65 7.65	5.22 5.20 5.20 5.50 5.50 5.50 5.14
Carbon.	81.93 80.05 80.07 80.41 77.97 77.97 77.49	82.61 79.71 83.64 82.01 80.78 77.65 75.53	76-09 81-36 76-94 79-82 79-58 80-08 74-55
Specific Gravity of Coals.	1.296 1.317 1.311 1.311 1.311 1.301 1.264 1.285 1.285	1.272 1.257 1.26 1.36 1.328 1.323 1.258	1.20 1.27 1.316 1.241 1.23 1.23 1.25 1.25
Locality or name of Coal.	Earl Fitzwillian's Elsecar         Hoyland Co.'s Elsecar         Hoyland Co.'s Elsecar         Butterly Co.'s Porland         Butterly Co.'s Langley         Stavely         Loscos Soft	Ince Hall C's Arley Haydock Little Def Balcarres Arley Inselection Hart Ince Hall Pemberton Yard Haydock Rushy Park Moss Hall Pemberton Four-fect	Wallsend Elgin

COAL.

Description of Coal.	Carbon.	Hydrogen.	lydrogen. Oxygen and Nitrogen. As		Density.	Observers.	
Alais, Dep. du Gard Rive de Gier—	89.27	4.85	4.47	1.41	1.322	)	
Grand Croix .	87.45	5.14	5.63	1.78	1.298		
Flenû from Mons	84.67	5.29	7.94	2.10	1.276		
Decazeville, Dep.							
Aveyron	82.12	5.27	7.48	5.13	1.284		
Epinac	87.12	5.10	11.25	2.53	1.353		
Commentry	83.72	5.29	11.75	0.24	1.319		
Blanzy	76.48	5.23	16.01	0.28	1.362	Regnault.	
Obernkirchen						Ŭ	
Lippe-							
Schaumburg .	89.50	4.83	4.67	1.00	1.279		
Céral, Dep., Avey-							
ron	75.38	4.74	9.02	11.86	1.294		
Neroi	63.28	4.35	13.17	19.20	1.410		
Saint-Girons	72.94	5.45	17.53	4.08	1.316		
Saint-Colombe .	75.41	5.59	17.91	0.89	1.305	J	
Leopoldinen-							
grube, Silesia .	73.88	2.76	2.47	21.89		ו	
Konigsgrube,							
Upper Silesia .	78.39	3.21	17.77	0.60	1.285	Karsten.	
Sälzer & Neuak,						axanstell.	
Westphalia .	88.68	3.21	8.11	0.70	1.288		
Hundsnak	96.02	3.20	6.45	0.60	1.338		

The composition of the ashes of a coal is in a great measure influenced by the nature of the rock in the vicinity of the seam from which it is extracted, as, besides containing the inorganic elements originally forming part of the plants, by the decomposition of which the coal has been produced, they will also to a certain degree consist of earthy particles, deposited in the pores of the coal by the infiltration of water from the overlying strata.

From the analysis of the ashes of seven varieties of British coals, I have obtained the results here given in a tabular form:—

Name of Coal from which the Ash was obtained.	Silica.	Alumina and Oxide Iron	Lime.	Magnesia.	Sulphuric Acid.	Phosphoric Acid.	Total.
Pontypool	40.00	44.78	12.00	trace	2.22	0.75	99.75
Bedwas	26.87	56.95	5.10	1.19	7.23	0.74	98.08
Porthmawr Rock Vein.	34.21	52.00	6.199	0.659	4.12	0.633	97.821
Ebbw Vale	53.00	35.01	3.94	2.20	4.89	0.88	99.92
Fordel Splint	37.60	52.00	3.73	1.10	4.14	0.88	99.45
Elgin Wallsend	61.66	24.42	2.62	1.73	8.38	1.18	99.99
Coleshill	59.27	29.09	6.02	1.35	3.84	0.40	99.97

Besides the above substances, traces of Chlorine were detected in most of the specimens examined.

# ANTHRACITE.

Anthractic, which is the oldest of all kinds of fossil fuel, is chiefly found in the transition formations. Its structure is perfectly homogenous, its fracture conchoidal, and its colour a jet black, with a vitreous lustre, which frequently displays a powerful play of colours.

<sup>1</sup> The results obtained by various chemists from analysis of specimens of this substance are given below.

Locality of Anthracite.	Carbon.	Hydrogen.	Oxygen and Nitrogen.	Ash.	Specific Gravity.	Observers.
Pennsylvania,			dinitie of		nesia di	
America	90.45	2.43	2.45	4.67	1.462	and states
Rolduc, near Aix- la-Chapelle . Mire, Bracon-	91.98	3-92	3.16	0.94	1.367	Regnault.
nière	91.45	4.18	2.12	2.25	1.343	11-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1-1
Sablé, Dep. de la Sarthe Vizille, Dep. de	87.22	2•49	3.39	6.90	1.751	
l'Isère	94.09	1.85	2.85	1.90	1.730	Jaquelin
Isère	94.00	1.49	3.58	4.00	1.650)	said all
Llanguicke, Gla- morganshire . Slievardagh, Ire-	91.44	3.84	3.58	1.52	1.375	Wright-
land ·	80.03	2.30	-	-	1.590	H. How.

Effects of Heat on Fuel.—Since all the various substances employed for the purposes of fuel are of organic origin, it follows that they are more or less prone to decomposition. Chemical combinations are stable within certain limits of temperature only, and when these points are passed, a series of compounds is produced by fresh groupings of the various elements of which the original substance was composed. When a substance such as wood is strongly heated, the arrangement of its elements is broken up, and new compounds are produced, capable of existing at the higher temperature at which they are formed. The nature of these products will in a great measure depend on the degree of heat which has been employed, as those obtained at one temperature will materially differ, both in quantity and composition, from those which are formed at another.

The results will moreover be essentially different, according as air is excluded from or admitted into the apparatus in which the heating takes place. When air is admitted, the products at first formed are immediately subjected to the powerful chemical action

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of the oxygen which it contains, and which combines with their elements to form new bodies, and combustion results as a secondary process.

If, on the contrary, the decomposition is effected by heat alone, with the exclusion of atmospheric air, the process is known by the name of dry distillation, and affords the means of collecting and studying the various products obtained at more or less elevated temperatures. This operation is of the greatest importance, not only from its occurring in all cases where a body is burnt, but also as affording the means of modifying various fuels, so as to adapt them to the particular circumstances under which they are When a piece of wood or coal is strongly to be employed. heated, its elements so arrange themselves as to give rise to gaseous compounds, and these escaping at an elevated temperature, ignite and produce flame. This combustion affords sufficient heat to cause the non-volatile portion, or carbon of the fuel, to combine with the oxygen of the air, which in its turn produces a fresh supply of gas from that portion of the mass with which it is in most immediate contact. In this way the combustion is supported until the substance is entirely consumed, as the heat evolved by the combustion of the carbon on the outer surface of the mass causes the dry distillation of the inner portions with which it is in contact, whilst the gases thus evolved tend to facilitate the union of the carbon of the outer surfaces with the oxygen of the air.

When the elements of which a fuel is composed are, by the aid of heat, forced to abandon their state of equilibrium, the nature of the new products obtained will be to a certain extent influenced by three different causes.

1stly. By the temperature by which the decompositions have been effected.

2ndly. By the degree of chemical affinity which exists amongst the various elements.

3rdly. By their relative degrees of volatility.

Hydrogen and oxygen are both volatile bodies, whilst carbon, on the contrary, is perfectly fixed, and therefore the two former will constantly have a tendency to separate from the latter, and pass off in the form of gas. Here, however, chemical affinity comes into play, and causes them to unite with each other and form new compounds, or to combine either singly or together with carbon, a portion of which is thereby made to assume the gaseous form. The most simple and stable compound of hydrogen and oxygen is water, whilst the excess of hydrogen which exists in all fuels takes up a portion of the carbon, with the production of light carburetted hydrogen or olefiant gas, and the united action of these continually tends to the formation of a series of ternary compounds, the nature of which will in a great measure depend on the temperatures at which they are formed, as those will be constantly produced which are most stable at the various degrees of heat attained. The rapid chemical action incident on the production of these varied compounds, necessarily produces a further elevation of temperature, and the consequent formation of new groups.

The number of compounds which can be thus obtained is extremely great, and appears to be only limited by the number of combinations, binary and ternary, which are mathematically possible for every amount of temperature. Besides these various gaseous products, the dry distillation of fuel affords acetic acid, pyroxylic or wood spirit, and tar, together with a number of other substances, such as, paraffin, picamar, pitacall, creasote, and naphthaline, &c., which are of less practical importance.

The greater the proportion of hydrogen contained in a fuel, and the less the quantity of oxygen, the more numerous are the combinations of carbon produced, but in no substance are these sufficient in amount to combine with the whole of the carbon present, a portion of which invariably remains in the solid form in the vessel in which the distillation has been effected.

The charcoal produced from wood, brown coal, and turf, always retains the form of the original fragment before it was subjected to the action of heat; and in the case of the former, its mechanical structure is so completely preserved that the year-rings and cells may be perfectly distinguished, and the kind of wood from which it was made ascertained.

Coal having a different elementary constitution, is differently affected by the action of heat.

Some varieties of coal, on being heated, undergo a kind of fusion, and yield a spongy residue or coke of a totally different structure from the coal from which it was produced. When small fragments of this kind of coal are subjected to the action of heat, they soften and adhere to each other, so as to form one mass, and from this property they have received the name of *caking coals*.

Coals which, by dry distillation, leave a coke retaining to a certain extent traces of its original structure, yet still having the property of caking on the fire, although in a less degree, are called *sinter coals*.

A third variety, which does not cake on the fire, and of which the finer fragments, when converted into coke, do not agglomerate, is called *sand coal*, and chiefly used for furnace purposes.

## PREPARATION OF ARTIFICIAL FUELS.

From the large amount of water contained in most varieties of fuel, as well as from the oxygen which enters into their constitution, it is evident that, when burnt, a portion of the heat evolved must be rendered unavailable, as the water present will not only earry off by its evaporation a part of the heat produced, but the union of the hydrogen and oxygen, forming part of the fuel itself, will give rise to another portion of water, which will have to be evaporated at the expense of a further sacrifice of heat.

In order, therefore, to obtain a larger amount of combustible matter in a given bulk of fuel, it has long been the custom to expel the aqueous and gaseous portions of such as are required to afford an intense heat, before applying them to the uses for which they are intended. This is the object of charring wood, or converting it into charcoal, which has since been extended to peat, lignite, and coal, in which latter case the process is called coking, and the resulting product is known by the name of coke. By this means, the different kinds of natural fuels are made to afford a series of artificial ones respectively richer in their heating properties than the substances from which they are derived; and their economical preparation, therefore, becomes a subject of great importance, not only to the metallurgist, but to all manufacturers who require the aid of an elevated temperature.

Manufacture of Charcoal.-If we ignite a small splinter of wood, and closely examine the way in which it burns when the lighted end is held downwards, two distinct periods will be observed. When the flame has become weak, from the volatile and combustible products having ceased to be evolved, except in very small quantities, it is observed to gradually die out, and nothing will remain but the feeble glimmering produced by the slow combustion of the remaining charcoal, which, not affording sufficient heat to admit of the combination of the carbon with the oxygen of the air, soon ceases. If, as soon as the flame is extinguished, the chip be placed in a close vessel, such as a testtube stopped by the finger, it will, from want of air, be quickly extinguished, without any of the glimmering before noticed; and if a piece of wood be at once heated in a close vessel, so as to completely char it without first producing ignition, the volatile matters are driven off, and charcoal produced without loss from In the ordinary methods of preparing the action of the air. charcoal on a large scale, both these principles are in a manner involved, as in this case a portion of the wood is consumed in

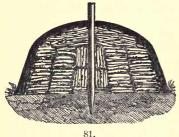
order to raise the temperature sufficiently to drive off the volatile constituents of that which remains, whilst the combustible products of distillation are invariably more or less perfectly consumed. Less frequently the coking is effected in large ovens or retorts, and in that case the second principle only comes into play.

Whichever of these contrivances be employed, it is, however, essential that sufficient time be allowed for all the hydrogen to combine with the oxygen so as to form water, without which these gases unite with, and render volatile, a portion of the carbon, and thereby diminish the amount of coke produced. Karsten, who has carefully examined this subject, obtained the following results, from which the advantage of the slow over the quick method of charring becomes apparent.

Species of Wood employed.	Per-centage Amount of Charcoal obtained by Quick Method of Charring.	Charcoal obtained by
Young Oak	16.54	25.60
Old do	15.91	25.71
Old do	14.87	25.87
Old do	14.15	26.15
Young White Beech .	13.12	25.22
Old do	13.65	26.45
Young Alder	14.45	25.65
Old do	15.30	25.65
Young Birch	13.05	25.05
Old do	12.20	24.70
Birch 100 years old .	12.15	25.10
Young Deal, P. picea D.	14.25	25.25
Old do	14.05	25.00
Young Fir, P. Abies D.	16.22	27.72
Old do	15.35	24.75
Young Pine, P. sylvestris	15.52	26.07
Old do	13.75	25.95
Lime-tree	13.30	24.60

The best method of ascertaining the quantity of charcoal yielded by the various kinds of wood is to place a weighed fragment of the wood in a crucible filled with saw-dust or charcoal dust, and having placed it in an assay furnace, the heat should be gradually raised to redness, at which temperature it is kept for about a quarter of an hour, when the crucible must be withdrawn from the fire, and allowed to cool previous to being opened. Fine sand may also be employed instead of saw-dust for the purpose of excluding the air from the wood. When the crucible has sufficiently cooled, the charcoal is withdrawn and weighed. This experiment should be repeated at least twice on each variety of wood, for the purpose of avoiding error.

Preparation of Charcoal in Meilers or Mounds.-The charcoalburner selects for this purpose a dry locality, sheltered, on at least one of its sides, either by a hill or a portion of the uncut forest; since, if the heaps were constructed in an exposed situation, it would be extremely difficult to prevent their being so acted on by the wind as to cause an unequal charring of the wood. When a proper situation has been chosen, and which, to prevent the expense of carriage, should not be far removed from the place where the wood is felled, a circular piece of ground of the diameter of the intended mound is marked out. If the soil be sandy and dry, this is done by merely cutting around it a shallow drain, for the purpose of carrying off the rain water which may fall during the process of carbonisation; but should there be any reason for suspecting the dryness of the soil, the surface is slightly raised by a covering of shingle, logs of wood, or the smaller branches of trees. The next operation is to cover the surface with the charcoal-dust or breeze obtained from a preceding operation, or, in default of this, a strew of leaves is sometimes employed. A long post or *quandel* is now driven into the ground in the centre of the circle, and it should be of such a length that its upper extremity may remain a little above the top of the intended mound. Around this, the wood, which has previously been cut into proper lengths, is piled, as shown in fig. 81. The greatest care is taken to avoid large cavities between the billets; and, for



this reason, those situated immediately around the quandel should be made by splitting the larger branches; in making the mound their thinner edges are placed towards the central post.

The more slantingly the billets are placed against this post, the greater will be the space between them; and, therefore, the more steeply they can be

piled consistently with the stability of the mass and the retention of the external covering, the better will it be for the subsequent

results. It is also evident that, when logs are piled horizontally in concentric circles radiating from the centre, considerable spaces must be produced by the divergence of the outer ends of the billets forming the various rings; and, therefore, a combination of the two methods, as shown in the figure, is frequently adopted. All unavoidable spaces resulting from the crookedness of the branches or their radiation must be carefully filled up with small fragments of wood; and when the surface has been thus made even, and the top or cap has been properly rounded by the addition of refuse wood, the meiler is provided with its moveable covering. This consists of turf, which is placed on the heap with the grassy side inwards, and beaten all over with a shovel, to make it lie closely on its surface. This is again covered either with damp breeze or sand, and the whole pressed down for the purpose of giving it solidity. The covering does not, however, extend to the foot of the pile, but is supported at a few inches from the bottom by twigs held in their places by forks, so as to form hoops around the lower part of the meiler. This open part at the base of the mound is for the purpose of allowing the escape of the aqueous vapours generated during the first stage of the operation, since no opening is allowed at the upper part of the pile, as it would tend to cause a draught, and consume a portion of the wood to be charred.

The dimensions of the mounds depend on circumstances incident to the neighbourhood in which the charring takes place, but should in no case be so considerable as not to admit of a good regulation of the heat. Heaps of only 10 feet in diameter are sometimes met with, but these are, generally speaking, inconveniently small, and mounds of from 30 to 40 feet across the base are, therefore, more frequently preferred, although in some localities meilers of even 60 feet in diameter are occasionally employed.

In arranging the billets around the central stake, care is taken to leave at bottom a small channel from it to the exterior part of the heap, and by means of this the fire is communicated to the pile, when it is finished, and the external covering has been well pressed down. Sometimes, instead of leaving this opening, the quandel itself is composed of three pieces of cleft wood so arranged and tied together with bands of green branches as to form a kind of chimney by which the fire may be communicated ; and in this case the horizontal passages become unnecessary.

When the mound is completed, and the covering securely packed down, fire is communicated to the centre of the mass either by throwing lighted coals down the vertical chimney, or introducing them by the horizontal gallery. For the purpose of facilitating the ignition, the wood placed immediately around the stake consists of the half-burnt charcoal, "charbon roux," resulting from a preceding operation, and which is picked out for that purpose as being more combustible than the ordinary wood of which the other parts of the meiler are composed. When the heap has been ignited, the hole by which the fire is introduced is tightly closed with turf and sand, or breeze; and the first period, called the *sweating*, during which the moisture is expelled from the wood, commences.

At this stage the greatest attention is necessary to prevent the explosion of the heap, either from the too rapid generation of vapour, or from the ignition of a mixture of atmospheric air with the inflammable gases produced by the dry distillation of wood. During the whole of the sweating process, large quantities of yellowish-gray smoke escape, particularly from the uncovered space at the base of the mound, and the interior of the covering becomes moist from the condensation of a portion of the aqueous vapour expelled from the wood by the action of heat. When the colour of the smoke issuing from the mound has been observed to change to a light grey, without any remains of the yellow tint beforementioned, the burner hastens to close the open space at the base and the charring period commences.

The covering of the meiler now requires to be thoroughly repaired, as the dry wood in the vicinity of the quandel will have become partially consumed, and have caused a sinking of the top or cap of the heap. The upper part of the covering is, therefore, rapidly removed, the charred wood forced down by means of a long pole into a compact mass, and the cavity thus made immediately filled up with fresh logs. The covering is now, with as great expedition as possible, replaced, and any crevices which may have occurred in it from the sinking of any part of the mound are stopped without delay, as they would otherwise, by admitting atmospheric air, cause the combustion of a part of the wood. The meiler is now left to itself for several days, except that small holes are from time to time made in that portion of the covering which is nearest the ground. This is done both for the purpose of allowing the escape of the tarry vapours, and also to admit the requisite amount of air, although the porosity of the covering of turf and breeze constantly aids in producing these results.

The dimensions of the heap have at this stage become considerably reduced, and care must be taken to observe whether it has equally diminished in all its parts, or whether some parts of its surface have sunk, whilst others are in their original condition, and thereby give an irregularity of outline to the meiler.

If such be the case, the charring has been badly conducted. This may to a certain degree be obviated, either by covering the

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sunken and more perfectly carbonised parts with an additional layer of turf, or, by means of an aperture made in the raised portions, the draught may be increased in that direction.

Towards the end of the process, and when the wood in the interior of the mound has become perfectly carbonised, it will be found necessary to adopt means to effect the charring of those portions which are in immediate contact with the moveable covering.

In this direction the wood is so cooled by radiation and by the condensation of aqueous vapours which issue from it, as to escape carbonisation; and the workmen, therefore, accelerate the draught in this part of the heap by making a second series of holes in the covering, above those which have been before described, but at a greater distance from each other. These are allowed to remain open until the smoke that issues from them is seen by its colour to be free from watery vapour; and, when this period has arrived, they are closed, in order to give place to others which are made at a short distance below them. Holes are never made for this purpose in the higher part or crown of the pile, as the draught is naturally in that direction; but in very large mounds, three, or even four, successive series of openings are not unfrequently made at different heights above the surface of the ground.

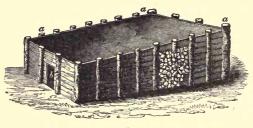
The time necessary for the operation chiefly depends on the size of the meiler. Small mounds are generally carbonised in from six to fourteen days; but if the diameter of the heap be more than thirty feet, at least a month is required for its completion.

If at the termination of the process the covering were removed, and the heap broken up whilst still hot, the access of atmospheric air would cause the charcoal to ignite, and the whole would be consumed. If, on the contrary, the covering were allowed to remain undisturbed until the mass had cooled down, so as to admit of its being removed without danger, much time would be thereby lost; and the charcoal is therefore withdrawn in small quantities, and with suitable precautions. In order to do this, the burner lays bare a space of two or three feet at the bottom of the mound, and, with an iron crook fitted to a wooden handle, withdraws, one by one, the logs of charcoal. These, which are red hot when drawn out, are either extinguished with water or by being buried in damp breeze; and as soon as the air begins to act too strongly on the exposed part of the heap, the opening is closed, and another made in a different part of the mound. This operation, which is repeated until the whole has been removed and extinguished, is best performed at night, since the slightest spark is then visible, and the chance of loss from the subsequent ignition of the charcoal is thereby reduced.

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In some parts of the Continent, another arrangement is employed for the preparation of charcoal. This process is known by the name of carbonisation in heaps or piles, and is said to yield charcoal of a better quality than that obtained from the ordinary meiler operation. For this purpose the logs are laid together in the form of a narrow wedge, as shown in fig. 82, of which the breadth is regulated by the length of the logs; its



82.

length varies from 20 to 30 feet. The thick end, which is farthest from that at which the fire is communicated, is from seven to nine feet in height, whilst the thin end is only about two feet above the level of the soil. In the erection of a heap of this kind, the burner commences by driving stakes, a, all round the parallelogram in which the logs are to be placed. These posts must project from the surface so as to be of the same height as the pile is intended to be at the point at which they are driven; and their outline, therefore, in every respect corresponds with the form of the pile itself.

These stakes are so placed as to leave a small space all round the wedge-shaped heap of logs which are piled within the enclosure. The billets used are usually seven feet in length; and, therefore, in order to allow a space of six inches between their ends and the sides of the enclosure, the latter is made eight feet in width. The opening thus left between the ends of the wood and stakes is for the purpose of receiving the covering, which, on account of the perpendicular sides, could not otherwise be kept in its place.

Boards or pieces of cleft wood are now applied against the inside of the posts, and wet charcoal powder or breeze is stamped down between them and the logs until the interval is entirely filled up. When this is done, the roof receives a triple covering of twigs, leaves, and, lastly, charcoal powder, which is moistened with water and well beaten down. In each of the long sides of the heap a series of holes is made in the boarding, but these do not penetrate through the charcoal coating; and in the lower end a larger one, b,

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is left for the purpose of igniting the logs, which is effected by first filling the aperture with shavings or dry wood, and then throwing some red-hot coals between the front posts and the pile of wood.

When the fire has fairly taken hold of the wood the aperture is closed, and other holes, of about three or four inches in diameter, are made at a height of about fifteen inches from the ground, in the same end of the heap. As soon as the smoke issuing from these assumes a clear blue colour, they are stopped, and others made higher up in the pile, which are in their turn closed as soon as the fire has sufficiently advanced towards them. By this arrangement the wood in the front of the pile is undergoing the charring process, whilst that placed behind is merely losing its volatile ingredients. When the operation is drawing to a close, it is found necessary to open a series of holes in the sides of the heap just above the level of the soil, as by this means the charring of the lower logs which constitute the bottom of the pile is effected. These, from their proximity to the ground, and the dampness deposited by the sweating of the wood, would otherwise remain as imperfectly charred billets; and, therefore, to prevent this, a series of holes is (when the heap is first constructed) cut in the planking forming the sides. During the early part of the operation these are closed by the breeze, which is closely packed between the boarding and the wood to be charred; but when the fire is required to descend to the bottom of the heap, the draught is made to pass in that direction by removing the damp charcoaldust from the apertures left in the planking. As soon as the logs in the front of the pile have become perfectly charred they are removed, and, being thus withdrawn from the action of heat at the moment the operation is finished, they not only yield a larger amount of charcoal, but that produced is also of better quality than if afforded by the ordinary meiler process.

In the foregoing operations the dry distillation of the greater portion of the wood which constitutes the heap or meiler is produced by the combustion of a certain quantity, which may be considered as the fuel necessary to produce the required heat. In order to conduct an operation with the greatest possible economy, care should be taken that no more air be admitted than is absolutely necessary for the combustion of this amount of fuel, as any further supply will cause a greater quantity to be consumed than is required for the dry distillation of the mass.

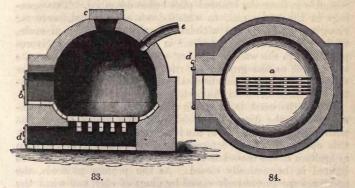
The success of these processes is also much influenced by the fact that the smoke and vapours, being evolved contrary to their natural course, are constantly made to take a downward direction, which not only affords the workman the opportunity of attentively watching the changes which are taking place, but also gives him time for taking the necessary steps to prevent the access of too large an amount of air. Ordinary wood loses from 20 to 25 per cent. of its bulk during the process of charring; and, therefore, the dimensions of the charcoal produced from a given quantity of wood is much less than that of the original meiler before the application of fire. This diminution naturally tends to produce cavities between the fuel and its covering, which, if actually formed, would become accessible to air, and thereby cause a useless consumption of wood; but in the case of the moveable coverings employed for this purpose, this inconvenience can never occur, as, in proportion as the size of the heap becomes less, through the shrinking of the wood, the covering will be found to sink with it, and is, therefore, much more effective in excluding air than any fixed roofing which could be substituted for it.

The loss arising from the combustion of a portion of the charcoal is also diminished by the way in which the charring is conducted. The mounds are always first lighted in the middle; and, therefore, the central portion of the heap will be completely charred before those parts which are in immediate contact with the covering have become much affected by the heat. In this way, the charcoal which has arrived at the last stage will, by the heat which it evolves, cause the dry distillation of the wood immediately around it, which, from the combustible gases evolved, and the burning of a portion of the wood in its vicinity, protects, by a zone greedy for oxygen, the portion already completely charred from the further action of air.

These methods have, however, the disadvantage of allowing the volatile constituents of the wood to escape, and these are more or less valuable according to the locality in which they are produced. Various plans have been proposed to prevent this loss. For this purpose it has been suggested that the covering of the meiler should consist of hurdles covered with clay, into which pipes for carrying off the volatile products could be placed: others have proposed that, instead of covering the heap with breeze or sand, slaked lime should be employed, so as to combine with, and thereby fix, the acetic acid produced. Both these plans have, however, been found to fail in practice, as the first destroys the flexibility of the covering, and the second is said to retain but a small portion of the acid produced.

If the method of carbonisation in long masses or piles be resorted to, instead of the meilers more usually employed, the gaseous and liquid products of distillation may be collected by an iron pipe placed in the highest end of the heap, which, being connected with a worm-tub filled with water, will discharge the condensed products in the liquid form. In cases where the site of the meiler can, without much inconvenience, from the facility of carriage afforded by sledges or a stream of water, remain stationary, the heap may be placed in a funnel-shaped pit, lined with clay, which, having at its lower part an inclined channel, either of iron or clay, will convey a portion of the impure acid and tarry matters into a reservoir, where they gradually accumulate.

**Charring in Furnaces.**—When the collection of the volatile constituents of wood is considered a matter of much importance, the charring is usually conducted in fixed furnaces, from which they may be conveyed by proper appliances into receivers adapted for that purpose. These furnaces are of two kinds. In the first the carbonisation is effected, as in the case of the common meiler, at the expense of a portion of the wood, which is consumed in order to produce the amount of heat necessary for the distillation and charring of the remainder. In the second variety, the heat necessary for the dry distillation of the wood is not obtained by the combustion of any part of the charge of the furnace, but is on the contrary raised by the application of a certain amount of fuel, which is entirely distinct from that from which the charcoal is to be manufactured.



Figs. 83 and 84 represent a section and plan of one of the many furnaces belonging to the first class. In this arrangement the air has access into the furnace through the bars, a. It is partially filled by the door, b, and when the charge has been raised to this level, the remainder of the wood is introduced through the aperture, c, which is left for that purpose in the crown of the arch. When the charging is completed, the openings, b and c, are closed by iron doors, against which earth is thrown for the

purpose of excluding the air. The wood is now ignited, by kindling a small fire in the ash-pit, immediately beneath the bars; and when it has become fairly alight, the draught is regulated by the sliding door, d, which admits of being opened or shut at pleasure.

As soon as the sides of the furnace have attained a sufficient heat to complete the operation, the door, d, is completely closed, and the furnace left to itself, until the whole of the wood which it contains is converted into charcoal. The volatile ingredients escape through the aperture, e, and are more or less completely condensed by passing through a series of tubes surrounded by water.

The grate at the bottom of these furnaces, instead of being made of bars of iron, is frequently a kind of trellis formed of brick-work or perforated tiles, and when the apertures in these are very small, the firing of the charge is effected through the door, b. When the operation is terminated, all the apertures by which air could be admitted are completely closed, and the furnace is allowed to cool; the charcoal being withdrawn by the door, b.

Furnaces of very different construction are in various places employed for the production of charcoal, according to this principle. Some of these are made quadrangular, and very nearly resemble in form the boarded piles before described. Two openings in the lower end, to which doors are adapted, serve for charging the wood, and withdrawing the charcoal when made, whilst the requisite supply of air is obtained through apertures perforated in the walls. The first row of holes is made on the same level as the ground on which the furnace stands; the second at eighteen inches from the floor; and the third at a distance of three feet from the first.

When the wood is placed in the furnace, a channel is constructed in the direction of its longer axis, which corresponds with one of the openings of the lower end of the building. By this opening the fire is communicated to the charge, and as soon as ignition of the mass has taken place, the door by which it was lighted is hermetically closed. As the process proceeds, the apertures are successively closed by plugs of clay, and when the operation is completed, the whole of the surface of the furnace is covered with that substance. The gaseous and other volatile ingredients escape from the furnace through a pipe placed in the higher end for that purpose, and when the charge has become completely charred, it is allowed to remain untouched until it has grown quite cold. In very large ovens of this description, the cooling often occupies from two to three weeks; since, if they were opened before being reduced to a proper temperature. the air, on coming in contact with the red-hot charcoal, would cause the greater part of it to be consumed.

Furnaces of the second kind, i. e. where the heat necessary for charring the charge is applied from without, are chiefly employed where the charcoal produced is considered to be of less value than the tar and other volatile ingredients, and they are therefore never used by the metallurgist for the preparation of the fuel he may require. The coniferous woods are found to yield the largest amount of tar, and are consequently those which are most frequently subjected to this kind of distillation. The arrangements by which both the tar and charcoal may be made available are extremely various, but one of those best adapted for the purpose consists of an iron cylinder, so set in brick-work that the flame and strongly heated air escaping from a fire placed below, may circulate freely around it. The wood to be charred is placed in the cylinder through an opening which may be closed hermetically. This is done by a luted door, and the vapours arising from the distillation are conveyed by an iron pipe into a wormtub, where those capable of assuming the liquid form are condensed. When the wood in the retort ceases to give off tarry matter, the luted door is removed, and the charcoal withdrawn by long rakes. On being withdrawn from the retort, it is placed in sheet-iron cases, which being furnished with close-fitting covers, prevent the combustion of the red-hot charcoal; and in these it is allowed to cool. By a more recent improvement in the construction of retorts of this description, the uncondensed gases issuing from the wood in process of charring are made to afford the amount of heat necessary for carrying on the operation. This is done by conducting the vapours which have escaped condensation by passing through the worm-tubs, under the bottom of the vessel, in which the wood is heated. When in this arrangement, by a fire placed under the retort, it has been raised to a certain temperature, and considerable quantities of combustible gases are evolved, they become ignited on coming in contact with the flame issuing from the grate, and thus afford sufficient heat for carrying on the operation.

The average quantity of charcoal produced by the meiler process from ordinary wood, amounts to about 22 per cent. When the distillation is carried on in close furnaces, this quantity is frequently increased to 27 per cent.; but as about 5 per cent. is required for heating the furnace, this method in reality affords results very little superior to those obtained from the common charcoal mound.

Mr. Mushet, who has made a series of experiments on the amount of charcoal yielded by different kinds of wood, obtained

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the annexed results. This investigation was conducted on a small scale, and the woods, before being charred, were thoroughly dried, and pieces of each sort selected as nearly alike in every respect as possible. One hundred parts of each kind were employed, and yielded the numbers here given.

Lignum Vitæ afforded 26.0 of charcoal, of a greyish colour, resembling coke.

Mahogany afforded 25.4 of charcoal, tinged with brown, spongy and porous.

Laburnum afforded 24.5 of charcoal, velvet black, compact, very hard.

Chesnut afforded 23.2 of charcoal, glossy black, compact, firm. Oak afforded 22.6 of charcoal, black, close, very firm.

Walnut afforded 20.6 of charcoal, dull black, close, firm.

Holly afforded 19.9 of charcoal, dull black, loose, and bulky.

Beech afforded 19.9 of charcoal, dull black, spongy, firm.

Sycamore afforded 19.7 of charcoal, fine black, bulky, moderately firm.

Elm afforded 19.5 of charcoal, fine black, moderately firm.

Norway Pine afforded 19.2 of charcoal, shining black, bulky, very soft.

Sallow afforded 18.4 of charcoal, velvet black, bulky, loose, and soft.

Ash afforded 17.9 of charcoal, shining black, spongy, firm.

Birch afforded 17.4 of charcoal, velvet black, bulky, firm.

Scottish Pine afforded 16.4 of charcoal, tinged with brown, moderately firm.

Messrs. Allen and Pepys obtained from 100 parts of the following woods, the quantities of charcoal as under—

Birch 15.	00   Oak	•				17.40
Mahogany 15	75 Fir					18.17
Lignum Vitæ 17:	25 Box			•	•	20.25

The results are generally less than those obtained by Mushet, who either operated at too low a temperature, or did not allow sufficient time for the escape of the volatile products.

The specific gravity of charcoal varies with the nature of the wood from which it has been manufactured, the denser varieties usually affording the heaviest charcoal, and vice verså. Henzel, who has made the most careful experiments on this subject, gives the following specific gravities for different kinds of wood-charcoal, Alder, 0.134; Birch, 0.203; White Beech, 0.183; Oak, 0.155; Red Beech, 0.187, and Red Larch, 0.176. Knapp, who made his experiments on a large scale, found the following numbers as the weight of a cubic foot of various kinds of wood-charcoal, interstices included:—Beech-wood charcoal (split wood) 8 to 9 lbs.; charcoal from split oak wood, 7 to 8 lbs.; pine wood, 5.5 to 7 lbs.; of the softer kinds of wood, 4.5 to 5.5 lbs.

The charcoal obtained from wood by the methods above described is not pure carbon, as, on being strongly heated, about 7 per cent. of volatile matter may still be driven off.

Charcoal has also the property of absorbing considerable quantities of water from exposure to the air. Messrs. Allen and Pepys found that by a week's exposure to a moist atmosphere, the charcoal of

Lignum Vit	tæ gai	ined i	n weig	ght	9.6 p	er cent.
Fir .					13.0	66
Box .					14.0	66
Beech .					16.3	"
Oak .					16.5	66
Mahogany					18.0	66

Besides this facility for uniting with aqueous vapour, charcoal possesses the property of absorbing a greater or less amount of the various gases. The following table by Saussure, shows the number of volumes of different gases absorbed in 24 hours by one volume of charcoal. In these experiments each piece was heated afresh to a red heat, and allowed to cool under mercury. When taken from under the mercury, it was at once plunged into the vessel of gas to be experimented on.

Ammoniacal gas .		·	1.14	11. 1	90
Hydrochloric acid gas	14. 16		·	1	85
Sulphurous acid gas .					65
Sulphuretted hydrogen				1	55
Nitrous oxide					40
Carbonic acid gas .			1.00		35
Bicarburetted hydrogen					35.00
Carbonic oxide					9.42
Oxygen			de la color		9.25
Nitrogen	19.1	1.10			7.50
Carburetted hydrogen					5.00
Hydrogen		1.		19.0	1.75

Brown Charcoal. Charbon Roux.—The object sought in the conversion of wood into charcoal, is to obtain a larger amount of combustible matter in a given volume of the fuel produced. One cubic foot of beech wood weighs 20 lbs., and, after deducting its oxygen and hydrogen, affords 9 lbs. of combustible matter: a cubic foot of beech charcoal, which consists almost wholly of combustible matter, weighs 12 lbs., and it is therefore evident that a given volume of charcoal will possess a heating power superior to that of the wood from which it is made, in the proportion of 4 to 3. It does not, however, follow from this circumstance, that, to obtain the largest possible amount of combustible matter in a given space, the carbonisation should be carried to its fullest extent. Berthier was the first to call attention to this point, and Sauvage, who fully investigated the subject, has proved beyond a doubt that the charring process, if carried too far, is attended with decided loss. In his experiments, 5 equal parts of air-dried wood were successively charred in the same furnace, and in each experiment the carbonisation was arrested at a different interval, for the purpose of examining the products obtained, both with regard to their state of carbonisation, and also their loss of weight and bulk.

From this examination he ascertained that if one cubic foot of wood contains an amount of combustible matter represented by  $908.^{1}$ —

1	cubic foot	charred during	3 hour	s will con	ntain 883. j	oarts.
1	66	"	4	66	904	66
1	66	66	5	"	1133·	"
1	"	66	$5\frac{1}{2}$	"	1091.	"
1	66	66	61	"	1136·	"
1	"	Mound char	coal	"	$1069 \cdot$	"

On inspecting the table, it is evident that the weight of combustible matter contained in a given quantity of fuel is not increased after the fifth hour, and that, if the charring be prolonged much beyond that time, a considerable loss is sustained. It consequently follows that the process may be advantageously arrested. before the wood becomes thoroughly converted into charcoal, and that the point should be sought at which it contains its maximum amount of combustible matter. In France and Belgium, this dried wood, or charbon roux, is extensively employed, and is prepared by a kind of mound carbonisation, but in which a somewhat different principle is employed. The heap in which the wood is placed is a lengthened pile, covered with earth, erected over a kind of channel passing through its axis. This is covered with iron plates, and at its outer extremity a fire is placed, the heated air of which is, by means of a ventilator, made to pass up the channel, and from thence, through a longitudinal slot in the iron plate, which covers it, into the heap itself.

The charring of the mound is regulated by its outer covering, so that when it is desired to elevate the temperature in any particular locality, the earth is removed from the part, and the draught thus allowed to pass in that direction. If, on the contrary, the carbonisation is found to proceed too rapidly in any part of the mound, the covering is thickened by the addition of more earth, and the action of the fire thus deadened. It is evident that this process is regulated by the same means, and governed by the same principles, as the ordinary meiler carbonisation; but great experience is required on the part of the workmen, in order to obtain the largest and at the same time the most uniform results. The adoption of charbon roux, instead of charcoal, effects a considerable saving of wood, and is on that account frequently advantageous; but it is found in practice extremely difficult to obtain it of a perfectly uniform quality, and as on this point its equality of action entirely depends, the working of the furnaces where it is employed is liable to become frequently deranged.

The workmen who attend a furnace can have no guide in making up their charges if the quality of the fuel is continually changing, and consequently the manufacture of charbon roux requires to be conducted with much greater care than is necessary in making ordinary charcoal, as in the one case the problem sought is the complete carbonisation of the wood at the smallest possible sacrifice of fuel, whilst in the other the charring should be arrested as soon as the fuel has attained its maximum calorific value; and as nothing but care and experience can ensure this, the process becomes one of considerable difficulty.

Peat Charcoal, or Peat Coke .--- The charcoal obtained from peat is, as far as its heating power is concerned, a valuable fuel, but it is nevertheless subject to disadvantages which prevent its application to ordinary purposes. In the first place this substance generally contains from 10 to 21 per cent. of ash, and yields from 24 to 30 per cent. of charcoal, which must therefore produce a very large proportion of ash, and is thus rendered entirely useless in, many operations to which it might otherwise be advantageously applied. If we suppose, for example, that a variety of peat contains 10 per cent. of incombustible matter, and only affords 25 per cent. of coke, it is evident that the coke thus produced would contain no less than 40 per cent. of ash, which would render it unfit for many of the purposes for which, if it were more free from ash, it might be employed. Besides this, it is found impossible to transport peat charcoal to any considerable distance from the place where it is prepared, for being extremely friable it soon falls to pieces, and is thereby rendered entirely worthless. In smelting furnaces, where it has to sustain the weight of the charges which may be above it in the series, this charcoal is also

found to crumble and choke the blast, and it can therefore be only employed under steam boilers or in forge fires.

Meiler Process.-From the circumstance of peat being cut in the form of rectangular bricks, it admits of being piled so as to leave but few interstices between the blocks; and from being less readily combustible than wood, the heaps in which it is prepared require a less perfect covering, and may be built of a smaller size. The mounds generally employed for making peat charcoal consist of from 700 to 1000 bricks, which are placed in heaps of from 5 to 7 feet in diameter, and 4 feet in height. After a proper situation has been selected for the mound, a post is firmly driven in the ground, and around this the blocks of turf are placed in concentric rings. At the bottom of the meiler four channels are made of the thickness of a brick, for the purpose of admitting air into the arrangement. These, which are at right angles to each other, commence at the central stake, and terminate at the periphery of the circle described by the base of the mound, and are subsequently used for regulating the rapidity of the carbonisation. When the peat has been properly arranged, the meiler is first covered with earth or charcoal dust, which is well packed down to exclude the air. Some dry wood for igniting the mass is then placed at the bottom of the stake, and the fire is communicated through one of the chambers before described. By the alternate opening and shutting of these, the combustion is equally effected in all the parts of the mound, and as soon as flames begin to appear from the crown of the heap, which for a small space around the stake is left uncovered, the opening is closed with turf and earth, and the completion of the charring is then accomplished by means of holes made all round in the covering, which commencing near the top are brought down by six inches at a time until they reach the bottom of the heap. In this process, like that of charring wood, the progress of the operation is known from the colour of the smoke evolved. Knapp states the produce in charcoal of the mounds examined by him to have been as follows:---

	Gave p. c.	Gave p. c.
	in weight.	in volume.
Peat, not completely air-dried	. 24 .	. 27
Peat, air-dried	. 27 .	$. 32\frac{1}{2}$
Peat, from Pfungstadt, very dry	. 30 .	. 29
Peat, of good quality, quite dry	. 35 <del>1</del> /2 .	. 49
From the district of Siegen, very good p	eat 23 .	. 40

The peat is withdrawn from the mound after it has been allowed to cool down to a proper temperature, as the use of much water for quenching it is objectionable, on account of the facility with which the resulting coke becomes reduced to powder. The amount of charcoal furnished by peat when the experiments are made on a small scale, is usually greater than those above given, as there is then less loss sustained from the crumbling nature of the product.

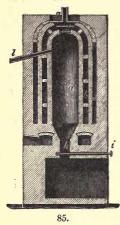
**Charring in Ovens.**—Although the products obtained from carbonisation in furnaces are not greater than those yielded by the ordinary meiler process, yet the supply of air and the rapidity of charring are more easily regulated, and consequently the operation is more cheaply executed, when ovens are employed.

One of the best forms given to these furnaces is that used at the manufactory of arms, at Oberndorf, in Wirtemberg, where it has been constantly used for the last fifteen years.

These furnaces, which have the form of an upright cylinder 9 feet in height, are closed at top by a circular arch, in which an aperture is left for the convenience of charging. This cylinder is  $5\frac{1}{2}$  feet in diameter, and has a fire-brick lining 15 inches in thickness. This is surrounded by the same thickness of sand, which is enclosed between the lining and another 15-inch wall, so that the entire thickness of the sand and walls together is 45 inches. Above the floor of the furnace are three tiers of air-holes made by inserting pieces of musket barrels in the wall, and which may be closed by bottle-stoppers from the outside.

The door for drawing the charcoal is placed on the level of the sole, and close by an iron slab, against which some sand is thrown for the purpose of excluding the air. On charging the furnace, a channel is left through its axis for the purpose of igniting its contents, which is done by throwing some lighted charcoal down the chimney thus made. At the commencement of the operation both the charging-hole and lower vent-holes are left open, but as soon as the peat becomes white-hot the former is shut by an iron plate, and covered with sand. The lower air-holes are at the same time closed, and those which are placed next above them opened. When all smoke has ceased to be given off, the whole of the apertures must be closed, and the furnace and its contents are allowed to cool together. The coking process is usually completed in from thirty to forty-eight hours, but the furnace is seldom fit to draw in less than six or seven days after closing all the air-holes. For this reason a series of ten furnaces are employed, in order to allow of one being charged and another drawn every day.

Instead of effecting the coking of one portion of the peat at the expense of another part which is consumed in the same furnace to obtain the necessary elevation of temperature, it is sometimes subjected to dry distillation in a kind of retort specially adapted to that purpose. At Courcy sur Ourcq, near Meaux, a well-constructed apparatus of this kind is employed. Fig. 85 is a sectional



view of this arrangement; a is the cylindrical coking chamber, the walls of which are heated by the flame and hot air passing through the intermediate flue, b. This space itself is divided by partitions of firetiles into three stages, through the apertures of which, the hot air from the fire, c, ascends and heats the coking chamber. In order to avoid loss of heat, a cylindrical hollow space, d, is left in the outer wall of the kiln, which, being constantly full of stagnant air, tends to prevent the cooling of the furnace. The peat is introduced through the opening at f, which, as soon as the charging is finished, is closed by an iron plate, and thickly covered with ashes or sand. The flue from the fireplace opens above this aperture, and its

outlet is provided with a moveable iron cover, g, in which there is a hole for the escape of the gases. The sole of the kiln consists of an iron plate, h, which, being attached to the iron rod, i, may be withdrawn or replaced at pleasure. When the carbonisation is completed, this plate is withdrawn, and the charcoal allowed to fall into the chamber placed below. The volatile products which are generated during the process are carried off by the pipe l, and conducted into a condensing apparatus.

The gases which escape from this are conveyed by metallic pipes into the fire-place, c, and being there consumed, yield a portion of the heat necessary for carrying on the operation. The products of charcoal obtained from this furnace are larger than those produced by the methods before described, but from the shock which it receives in falling from the retort to the chamber beneath, it frequently becomes much broken, and is thereby rendered to a certain extent less valuable than if obtained in larger masses.

**Charring Brown Coal**—Brown coal is of all kinds of fuel the least adapted for carbonisation; for although it is acted on by heat in the same way as wood, and produces a combustible charcoal, yet it is subject to inconveniences which render its production from this substance too costly for general application. Lignite, like peat, contains a large proportion of ash, and this per-centage will necessarily be much greater in the charcoal produced than in the coal from which it is made. This, from the tendency which the charcoal would have to clinker on the fire, prevents its being used for many purposes for which a fuel of greater purity could be employed. In addition to this, the action of heat causes the layers and concentric rings which are scarcely perceptible in the lignite to separate from each other, and the charcoal manufactured is thereby either reduced to such small fragments as to be of little service as fuel, or is rendered so extremely friable as to be unable to bear carriage even to a short distance from the locality where it is produced. The carbonisation of lignite in mounds is, however, carried on on a small scale in the neighbourhood of Cassel, but the situations where this can be done with advantage are far from numerous.

The following results were obtained by heating pieces of brown coal in close crucibles until all traces of their volatile constituents ceased to be evolved :<sup>1</sup>—

10	0 Parts of								Ga	ve of charcoal
Earthy Coal	from the Ba	sses	A	lpes	3					48.5
Lignite from										38.9
"	Friesdorf .									28.2
66	Iceland .									57.5
"	Auszig .								8.1	40.1
66	Orsberg .									62.8
66	Hegendorf						1			41.2
66	Stöszchen									29.1
66	Pützchen				1.0					46.4
66	"								3.6	44.7
"	Neundorf	1.15		-						38.4
66	Coulang .									38.1
66	Jahnsdorf									32.8
66	Hartenberg					5				37.2
66	"		1							34.6
66	Kanden .			6						37.5
Pitch Coal fr		m								38.1
"	66			10						29.3
"	Altsattel .			:						40.3
Lignite from								·	1	35.6
	· Ortera · ·	•	•	•	•	•	•		•	000

#### COKE.

The combustible residue which remains after the volatile constituents of pit-coal have been eliminated by the action of heat, is called Coke. In making this substance, as in the manufacture of charcoal, one of the objects sought is the production of a fuel which

<sup>1</sup> Knapp's Technology, vol. i. p. 54.

shall contain in a given bulk a larger amount of combustible matter than exists in the coal from which it is obtained.

Good coke should also possess sufficient solidity to enable it to withstand the pressure of a smelting furnace without crushing, and is of little value unless obtained in large pieces not liable to crumble and form dust. From the difference observed in the properties and composition of coals, it is evident that all cannot be fitted for the manufacture of coke, and it is therefore necessary to select such as yield that best adapted for the purposes of the arts.

Sand coal, from the friable nature of the coke which it produces, is not adapted for this purpose; whilst if a too easily caking variety be employed, it is found to yield a spongy coke very liable to crush. This arises from the compression of the cells which are formed in the softer coal by the escaping gases, and a coal should therefore be chosen, which, although less brittle than the sinter kind, is less liable to melt on the fire than that commonly known by the name of caking coal.

The nature of the coke produced from any particular variety of coal is also considerably influenced by the method of its preparation, as well as, in a certain degree, by the nature and amount of the ash existing in the coal from which it is manufactured. Coke which has been made in large quantities at a time is usually better than that manufactured on a more limited scale, as, from the weight of the mass operated on, the product will be more compact than when smaller quantities are used, whilst, from the high temperature obtained, the volatile ingredients will be more perfectly driven off. When the ash contained in the coal is fusible, it melts and forms a kind of cement for the particles of coke, which is thereby rendered more compact, and less liable to be crushed by pressure.

From the circumstance of coal being constantly raised in the same localities, the manufacture of coke is usually carried on in stationary apparatus, but from its being but slightly inflammable, and requiring a good draught to effect the combustion, its production even in the open air becomes an easy operation.

**Carbonisation in Heaps.**—The earliest method of manufacturing coke, and one still employed in the present day, is carbonisation in heaps. When this process is resorted to, no external covering of the mound is used, and the coking, which is at first carried on with free access of air, is finally checked by the application of a coating of breeze or earth when the coke has already been produced. The coke meiler is always erected on the same station, which soon becomes covered with a sufficient amount of breeze for the purpose for which it is used.

Instead of making round heaps like the ordinary forest meiler, for the production of charcoal, a long rectangular mass is generally preferred, as by this means a much larger amount of coal can be operated on at one time. The length of these piles is frequently from 150 to 200 feet, and in order to erect them, a line is first stretched in the direction of the axis of the heap throughout the whole length of the coke station. Large pieces of coal are now placed on either side of this string, so that by coming together at the top they form a kind of triangular gallery, running the whole length of the intended meiler. In making this central channel, it is of importance that the fragments should be so placed as to be upright with relation to the layers of deposition, whilst the fractured surfaces must be placed at right angles to the axis of the meiler. A second series of blocks of coal is then placed on the first, and these are again covered with others similarly arranged, but of gradually decreasing size, until the heap has attained a width of six feet on either side of the central channel, when the whole is covered with a coating of smaller coal about two feet in thickness, which is arranged without any regard to its stratification, although care is taken that the larger fragments be placed on the sides of the mound, the top being covered with small dust only. In order to ignite the heap, stakes are driven at regular intervals from the top of the pile to the central canal, and these being withdrawn leave a series of chimneys into which burning coals are introduced. The fire is thus communicated to the mass in so many points at the same time, that ignition soon becomes general, and the coking commences through its whole extent.

The person in charge of the operation has now to prevent the action from advancing too far, and as soon as he observes that thick smoke and flame have ceased to be evolved from any particular part of the mound, and also that it begins to get covered with a coating of ash, he immediately prevents any further action by covering the flame with breeze, which being closely packed down prevents the entrance of air, and quickly deadens the fire. As the coking advances this is repeated until the whole heap is covered down, when it is allowed to remain two or three days to cool, care being taken to supply it with a thicker covering on the side which is exposed to the wind than on that which is opposite. When the fire is nearly extinguished the coke is withdrawn and subsequently cooled by the use of water. This method of making coke, although extremely simple, is far from being economical, for inasmuch as the charring commences on the outer and upper parts of the mound, and then gradually proceeds towards the central and lower portions, it follows that the surface of the heap is coked before the central parts are reached, but which must be

fully charred before the air can be excluded. The outside of the meiler is therefore burning to waste without the possibility of its being prevented, and the central portions are but little acted on at the time that the surfaces are being uselessly consumed.

**Coking in Mounds.**—A more economical method of making coke than the one which has just been described, is that represented in the annexed woodcut, fig. 86. A chimney of about



three feet diameter at bottom is loosely built with bricks on the site of the intended meiler, B B. The brick-work of this flue has a number of holes, b, made by here and there

leaving out a brick, and the upper part, which is enclosed with solid work for a short distance near the top, is provided with an iron cover. Around this chimney the coals to be coked are placed in a slightly inclined position; the largest masses are piled nearest the centre of the mound, and the dimensions of the other pieces gradually reduced towards the outside of the heap. A meiler of this kind is generally about 25 feet in diameter, and 4 or 5 feet in height; and when completed its surface is covered with a coating of breeze four or five inches in thickness, which is well packed down for the purpose of excluding the air. A shovel full of burning coals is now introduced through the perpendicular chimney, which soon communicates with the heap through the various apertures, b, and the mass gradually becomes ignited, beginning from the bottom and centre, and from thence spreading in the direction of the covering of cinders. Openings made in the foot of the meiler admit of a certain quantity of air passing through and escaping by the chimney. At the expiration of four or five days the fire will have reached the covering, which then becomes red hot. The top of the chimney is now closed by an iron plate, and the apertures at the foot of the pile are at the same time shut by a little coke dust tightly compressed. After being allowed to remain for two or three days, the coke will have sufficiently cooled, and may be then drawn and quenched with water.

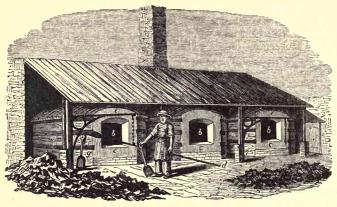
In some localities no covering is applied to these meilers, and when the burning coals are thrown into the central aperture, the combustion is carried on by the air, which on all sides enters freely through the crevices occurring between the fragments of coal of which the heap is composed. When any part of the mound becomes coated with ash it is immediately covered with breeze to protect it from further action, and as soon as the whole surface is thus attacked, the iron plate is placed on the top of the chimney, and the mound allowed to cool.

By this method a less per-centage of coke is produced than is obtained from that now to be described; but it has still one advantage over the ordinary heap—viz., that the coking proceeds from the centre towards the circumference, which is not the case in the old process.

**Coking in Ovens.**—The foregoing methods of making coke are gradually becoming superseded by oven coking, and this more particularly in those localities where, the price of coal being high, it becomes a matter of importance that as small a portion as possible be lost during the operation. The furnaces used for the production of coke are invariably heated by the combustion of a portion of the fuel with which they are charged, and not at the expense of a distinct quantity, specially consumed in a separate fire-place, for the purpose of raising the temperature to the requisite degree.

When, on the contrary, coal is charred in order to obtain the gaseous products of its distillation, and the coke made is only regarded as a secondary product of the manufacture, the operation is carried on in close vessels heated by distinct fire-places; but in this case the coke produced is spongy, and consequently quite unfit for metallurgical purposes.

The ovens employed for the manufacture of coke vary so much in form and dimensions that it would be impossible here to give even a brief description of all those which are in general use; but the principle involved being the same in all cases, it will be sufficient to explain the construction and management of some of those most frequently employed. Fig. 87 represents a coke furnace of a very common form. The cavity of the oven, which is about 9 feet in diameter, and 3 feet 6 inches in height, is internally lined with fire-bricks, well jointed in refractory clay. The form of the furnace closely resembles that of a compressed beehive, and at the top of the dome is a circular aperture or chimney, a, which can be closed by an iron plate. A slightly arched doorway of about 21 feet square is also left at b for the purpose of charging the oven and withdrawing the coke. This opening is strengthened by a heavy cast-iron framing, c, which is built into the brick-work and secured in its place by iron girders. Where large quantities of coke are manufactured, these ovens are placed back to back in double rows, with a series of charging doors on either side of the long mass of masonry which surrounds them. The charge of each is about three tons of coals, which are thrown into them through the door, b, and as this is done immediately after the withdrawal of the former charge, and whilst the oven is



87.

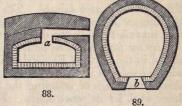
still extremely hot, the coal soon begins to give off large quantities of inflammable gases, which escape through the aperture in the top of the dome. When the charging is finished, the doorway, b, is closed by fire-bricks loosely piled up, but the air has still free access into the furnace through the openings left in the stopping, which supplying the necessary oxygen to the gases evolved, they soon ignite, and the temperature of the oven and its contents is rapidly raised. At the expiration of three hours the lower holes in the loose brick wall are closed, to prevent the access of too much air, which still finds its way through those which are above, and escapes by the chimney. In some instances, instead of closing the charge hole with loose bricks, an iron door lined with tiles, and provided with draught holes, is employed. These are successively stopped by lumps of clay, and when it is required to exclude the air entirely, it is done by applying a sheet of iron against the bricks, and luting the edges with clay.

In twenty-four hours after charging, the upper holes are also closed by plastering them over, and the furnace is allowed to remain twelve hours with the chimney open, during which time the remainder of the gaseous matter is expelled by the heat, and passes off in flame by the opening in the dome. When the flame emitted from the chimney ceases, which usually occurs at the expiration of another twelve hours, it is covered with an iron plate made tight by a layer of sand, and the whole is allowed to stand for twelve more hours, for the purpose of moderating the heat of the furnace and its contents.

At the expiration of forty-eight hours from the time of charging, the oven will be sufficiently cool to admit of drawing, and the door may be now opened without causing much loss by the burning of the coke. A large iron shovel, d, called a pelle, suspended by a piece of chain to the crane, e, is now thrust between the coke and the bottom of the oven, and as the weight on the blade will be supported by the crane which turns on its axes, a large mass can be taken out with but little exertion on the part of the workman. The swinging of the small iron crane enables the burner to place the heated coke on any part of the paved floor within the circle described by its extreme end and the point of suspension, and as soon therefore as it is withdrawn it is strewed thinly on the ground, and rapidly cooled with water. When it is thus extinguished and has become nearly cold, it is taken up in a grated shovel, g, and transported by means of iron wheel-barrows either to the place where it is stacked, or to the furnace in which it is consumed. The grated shovel is used to separate the breeze from the large coke as the former falls through the intervals between the bars, so that the latter only can be taken up and placed in the barrows. Iron is used in preference to wood for making the barrows, both on account of its being incombustible, and also because wooden ones would sooner become destroyed by constant friction against the hard and rough edges of the coke.

Fig. 88 represents a vertical section, and fig. 89 a ground plan of a furnace of this kind.

Various contrivances have at different times been employed to facilitate the cooling of the ovens, during the last stage of coking: but very few of these have come into general use, as the increased ex-



pense incurred in adapting them to the furnaces is in most instances more than equivalent to the advantages to be derived from their use. One of the best methods of hastening this cooling of the coke is the construction of furnaces with air flues, not only under the refractory lining of the bottom, but also around the sides of the oven. During the first stages of the process, all connection between these and the external air is cut off by iron dampers, but as soon as it is required to cool down the oven for the purpose of drawing the charge, the air is admitted by side openings, and escapes through a set of holes left for that purpose in the upper part of the brick-work. This causes a draught, and the constant influx of fresh quantities of cold air, which, by reducing the temperature of the walls of the oven, materially shortens the usual period allowed for cooling. Where many ovens are employed, and in localities where it is desirable that the smoke produced should be carried as rapidly as possible from the neighbourhood of the furnace, a long flue is constructed along the top of the whole range, and by this the smoke and fumes issuing from the openings in the crowns of the ovens are carried to a suitable chimney. In this case the apertures, instead of being closed with an iron plate as above described, are shut by sliding dampers worked either by a lever or by a pulley and counterpoise.

The ordinary routine of coke-making has to a certain extent been modified by the Messrs. Cory of Lambeth, who in their factory are in the habit of cooling the coke in their ovens before it is drawn. This is done by well watering it as soon as the operation is completed, with a jet supplied by a powerful force pump. This is said not only to effect a saving by preventing any loss by combustion during the time the charge is being withdrawn, but also, by the decomposition of the water, to carry off any remains of sulphur in the form of sulphuretted hydrogen, and sulphurous acid gases. Care is of course taken that the furnace be not so far cooled as to be unable to inflame the succeeding charge, and as the whole of the water is converted into vapour before reaching the sides of the furnace, the brick-work is not in the slightest degree injured. The coke which is thus cooled in the furnace is also said to be brighter and more sonorous than that manufactured in the ordinary way.

Another form of these furnaces is much used among the coal mines in the north of England. This arrangement is that commonly employed in the neighbourhood of Newcastle, and has the double advantage of retaining the heat, and requiring but little brick-work for its construction. Each single furnace is a square ten feet deep, twelve feet wide, and ten feet high. The top is arched, and the whole thickness of the side walls, including the internal lining of fire stone, is but two feet. In the centre of the arch an aperture  $2\frac{1}{2}$  feet square, and lined with a cast-iron ring, is left, whilst another is made on the level of the floor for introducing the coals to be coked. This opening is supplied with an iron casing which forms a groove in which the door slides. The door, which consists of an iron framing filled with brick-work, is suspended by a chain, and raised or lowered by a lever. In the brick-work of the door are left several openings, which are, however, sometimes dispensed with, and in this case the bricks are loosely placed in the frame, and admit sufficient air through the crevices between them for the combustion of the gases issuing from the coals.

The charge of each of these ovens is about two tons, and requires to remain about 48 hours in the furnace before it is in a fit state to be drawn, which is done by an iron hook used specially for that purpose. In all other respects these ovens are managed precisely like those last described, fresh coal being thrown on as soon as the coke is withdrawn, and a certain amount of air admitted during the former part of the operation.

In this country large quantities of tar are annually furnished by the distillation of coal, from which gas for illumination is obtained, and as the supply may be considered equal to the demand, the price of this product is so extremely low as to offer but little inducement to the manufacturer of coke to take measures for the collection of that which is constantly being driven off from his ovens in the state of vapour. In some localities, however, the case is very different, and from the high price obtained for tar, it becomes a matter of the greatest importance that as small a portion as possible of this fluid be allowed to escape condensation.

At Gleiwitz, in Silesia, the furnaces used for this purpose are cylindrical ovens eight feet high, and about six in diameter. The upper part of this oven is arched over, and has an opening for the escape of gases, which may be closed by an iron plate, as in the furnaces before described. The charging door, which is on a level with the sole, is closed by piling up loose bricks, and afterwards made air-tight by applying an iron door on the outside, and stopping the interstices with clay. Besides these doors the furnace is also provided with a series of air-holes made through its walls at different heights from the floor, and a large iron pipe is fitted into the arched brick-work of the top for the purpose of carrying off and collecting the tarry vapours which are evolved. These, together with the gaseous products, are conveyed to a cistern which condenses and collects the former, and allows the latter to escape. In the cold season this pipe leads directly to the receiver, but during warm weather it is connected with a series of zigzag pipes, which, passing through cold water, act as a refrigerator and aid the condensation. The charge of one of these furnaces is from 35 to 40 cwt. of coals, and as soon as it has taken fire the larger openings, and all the air-holes, except the lower row, are closed. When the fire, as seen through these apertures, has assumed a reddish-yellow colour, they are closed, and those opened which are immediately above them. On closing the second series of holes, the third is opened, and so on until the whole charge has been sufficiently and regularly ignited. The first and second rows of holes are each allowed to remain open ten hours, the third sixteen hours, and the fourth and last series three hours, after which the oven is allowed to remain twelve hours to cool, and the coke then drawn and quenched with water.

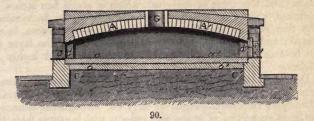
The coal used in these ovens is slightly caking in its character, and each charge, besides yielding 53 per cent. by weight, or 74 per cent. by volume of good coke, produces on an average  $5\frac{1}{2}$ gallons of tar. The same coal charred in meilers affords only 47 per cent. of its weight of coke, and this far more spongy and friable in its nature than that obtained in furnaces. It is also probable that ammonia might be manufactured with advantage from the water associated with the tar thus obtained, although it does not appear that it has yet been collected for that purpose. In this country the low price of tar has prevented the introduction of furnaces on this principle, but it may be considered certain that by the adoption of properly constructed ovens large quantities of the volatile alkali might be collected at a very small additional expense.

It is evident that the ammoniacal vapour must be principally evolved during the first stage of the coking process; and, consequently, if for a short time after charging the furnaces the doors were securely closed, and the gases and vapours escaping from the coal conducted through a proper refrigerator, nearly as large a proportion of ammonia should be obtained as would be procured from the same fuel during the manufacture of coal gas by the ordinary method.

Good coke may also be manufactured from the small particles and dust of those varieties of coal which have the property of partially melting and caking when strongly heated. These small fragments will, on being charred in properly constructed apparatus, adhere so firmly to each other as to form coke quite equal to that produced from the larger pieces. At St. Etienne a trial was first made by pressing the moistened small coal into large boxes provided with moveable pegs corresponding to the channels and air-holes required to effect the coking. These cases were so constructed as to admit of being easily taken to pieces after the coal had been properly forced in, and, as the pegs were at the same time withdrawn, the coal was thus moulded into a small meiler provided with all its necessary flues and channels. This process was found to yield very good firm coke, but the amount of labour required to form the mound proved to be too expensive to admit of being advantageously employed, and was consequently abandoned in favour of the furnace, fig. 90, which will be now described, and which is that at present used at Rive de Gier, on the Loire, for coking fine coals.

This furnace is constructed on the same principle as an ordinary

baking oven, and consists of a flat arched space with an even sole. Like those before described, it is without a distinct fire-place, and



the heat retained by the walls of the apparatus after the withdrawal of one charge is sufficient to cause the ignition of that which succeeds it. The floor, a a', of this oven is an oval space, 111 feet wide, and 23 feet in length, composed of a bed of fireclay six inches in thickness, spread out and well beaten on a layer of loose stones, b b'. This, again, rests on a mass of rubbish and gravel, C C', with which the centre of the foundation is filled up, and which forms the immediate support of the bottom of the furnace. For the purpose of charging and withdrawing the coke, two openings, d d', are placed opposite each other at the extremities of the lesser axis of the furnace : these are closed by doors, two feet high, and two feet eight inches wide, made of iron, lined with fire-bricks, which are turned towards the oven. Each of these door-ways is provided with cast-iron linings, e e', made with grooves, in which the doors slide when raised or lowered by means of the chains and levers to which they are attached. In the middle of each of these doors is a small opening, through which the workman can observe what is going on inside the furnace, and thereby regulate his proceedings. The greatest distance from the roof to the sole is four feet. A small chimney, G, one foot six inches in diameter, and one foot five inches in height, is placed in the centre of the dome, A A', for the escape of gases.

The whole of the internal lining, except the floor, is composed of fire-bricks, and the arch jointed with clay instead of lime, in order to render it better calculated to withstand the heat produced. The outside of the furnace may be of either brick or stone, but should be covered with a good layer of mortar mixed with sharp sand, for the purpose of excluding the air which might otherwise enter through the jointings of the work. Should any crack occur during the working of the apparatus, it is for the same reason carefully stopped with clay kept prepared for that purpose.

The furnace is charged while still hot from the preceding operation, and the layer of coal-dust, which is about ten inches in thickness, should be evenly spread on the sole by iron rakes. The fine coal is slightly sprinkled with water before being heated; and, if it be of a very caking description, the layer on the bottom of the furnace should not exceed eight inches in thickness.

During the first two hours after charging, the doors are entirely closed, with the exception of a small slit at the bottom, which affords just sufficient draught to carry off, through the chimney, the large quantities of gases and vapours which escape from the charge. This stage of the operation corresponds to the sweating period of the charcoal mounds, and it is found that the more slowly and regularly this is conducted, the larger is the amount of coke produced.

The charge of one of these ovens varies from 60 to 70 cubic feet, according to the more or less caking nature of the coals operated on. At the expiration of two hours, after charging, the evolution of vapours rapidly declines, whilst the quantities of inflammable gases given off are much increased. After a short time, these, mixing with the atmospheric air entering beneath the door, suddenly ignite with a sort of explosion, and the yellow smoke which has hitherto been evolved through the aperture in the dome is quickly replaced by a cloud of a much darker colour. At this point the charge is at a dull cherry-red heat, and it becomes necessary to increase the temperature, in order to expel the last traces of volatile matter. This is done by raising the door about three inches from the bottom jam of the frame, and the fire soon draws up and yields an increased quantity of dusky-coloured smoke. At the expiration of three quarters of an hour, the smoke gets clearer and less sooty, the heat of the charge becomes uniform in all parts of the furnace, and the coal begins to split into large columnar fragments. At the end of three hours from the first opening of the door, the mass of coke is usually split from the surface to the sole of the furnace, and at this stage of the operation the doors are closely shut, and the crevices stopped with fire-clay. The heat, which is, as it were, shut up in the walls, will now be sufficient to complete the charring of the coals, and the expulsion of the last traces of gaseous matter is effected by the same means. After thus shutting up the furnace, the flame issuing from the central chimney still flickers for a short time over the opening, but gradually becomes more and more feeble, until it finally dies away altogether. The top of the chimney is now closed by an iron plate, and the coke

drawn with as little delay as possible, in order to prevent loss of heat before the introduction of another charge of coal. Each operation requires twenty-four hours for its completion, and as soon as the coke is withdrawn, it is sprinkled with water, for the double purpose of cooling it more rapidly, and also of producing the decomposition of the sulphur compounds which might otherwise be retained, and render the coke of less value as a fuel.

When one charge is withdrawn, another is placed in the furnace, and the process goes on without intermission until it is necessary to allow the oven to cool for the purpose of examining its refractory lining, which, if made of good bricks, will require to be repaired about once in six months. This process yields better results than any of those before described. At Rive de Gier, the annual produce of coke is found to amount to 69 per cent. of the coal employed, and even the worst varieties, which are there subjected to the coking process in these ovens, afford from 60 to 65 per cent. of coke, whilst in the mound from 45 to 50 per cent. only is obtained, and in the heap even rich coal rarely yields more than from 40 to 45 per cent.

It is found by experience that coke produced in the furnace is denser than that obtained either in mounds or heaps; but, on the other hand, it contains a larger amount of sulphur, and is, on this account, less adapted for certain purposes in which that substance is prejudicial than that prepared in the open air. On cooling, good coke splits into long prismatic masses, in some degree resembling basaltic columns. Its colour is a kind of steelgray, almost approaching in some instances to silvery whiteness; but the surfaces of many varieties are covered with an iridescence supposed to be dependent on the presence of sulphur, and is therefore a property by which its value is by no means enhanced. Like charcoal, coke absorbs moisture from the air. This in damp weather sometimes amounts to 30 per cent. Coke which has been for a long time exposed to the air and damp, becomes soft and friable, and is, therefore, ill fitted for many purposes to which otherwise it might be applied.

#### COMPARATIVE VALUE OF FUELS.

It must be evident to every one who has observed the combustion of different fuels, such as wood, peat, charcoal, pit-coal, and coke, that, to produce a given calorific effect, very varying quantities of these substances must be consumed. This difference, although less apparent between distinct specimens of the same kind of fuel, is, however, quite appreciable when the effects produced by the combustion of a given weight of each variety are carefully compared.

Various methods have at different times been employed for the purpose of measuring the relative amounts of heat produced by the combustion of equal quantities of fuels of varying composition; but as the heat evolved can in no instance be directly estimated, the calorific values of the substances examined must in all cases be judged of in accordance with certain physical or chemical effects produced on a third body.

In order to ascertain the heating power of any substance, the knowledge of two things is necessary,—the amount of heat which it is capable of producing, and the time necessary for its development. The results thus obtained are usually known as the *theoretical effects* of the fuel. Since it is impossible to ascertain the real amount of heat generated, the economic value is always judged of by comparing its effects with those produced under precisely similar circumstances by other varieties. These comparative estimations may be effected in various ways, all of which are sufficiently accurate for practical purposes. The more ancient experiments on this subject were all conducted on the same principle, and are exclusively physical in their character.

The instrument employed for this purpose was called a calorimeter, and the amount of heat produced estimated either in accordance with the quantity of ice melted, or the weight of water elevated to a certain temperature by the substance operated on. Both these methods are, however, precisely similar in principle, and, from the following considerations, it becomes easy to give the same expression to the results obtained by either modification of the instrument. It has been found by Lavoisier and Laplace, that the quantity of heat required to melt one pound of ice is just sufficient to elevate the same weight of water from 0° to 75° C.; or, what is precisely the same thing, to raise 0.75 lbs.<sup>1</sup> from 32° Fahr. to the boiling point. Clement and Desormes have also shown that a given weight of aqueous vapour, whatever may be its temperature or tension, is always produced by the same quantity of heat; and therefore contains, and is capable of again yielding to other bodies, an exactly equal amount. Moreover, according to the same authorities, the heat absorbed so as to no longer affect the thermometer (latent heat) during the conversion of water into steam is 5.5 times<sup>2</sup> greater in quantity

<sup>1</sup> According to the more recent experiments of Regnault, this number must be raised to 0.79.

<sup>&</sup>lt;sup>2</sup> According to Rumford, 5.67.

than that which is required to raise the same weight of water from 0° to 100° C.; and it therefore becomes easy to calculate how much water could be evaporated from its boiling point by the quantity of heat necessary to melt one pound of ice. This will be found equal to  $\frac{0.75}{5.5} = 0.154$  lbs. of water.

The following table, extracted from Knapp's Technology, gives the results of Count Rumford, as obtained by his water calorimeter :---

One Pound of the following kinds of Wood, when burnt, will heat	Pounds of Water from 32° to 212°.
1. Limetree wood.	
Dry wood, 4 years old	. 34.707
" " slightly dried	. 38.833
" " strongly dried	. 40.131
2. Beech wood.	. 10101
	. 33.798
Dry wood, 4 or 5 years old ""strongly dried	. 36.476
	. 00 470
3. Elm wood.	00.005
Wood dried, 4 or 5 years old	. 30.205
" strongly dried	. 34.083
" dried brown	. 30.900
4. Oak wood.	
Common fire-wood, in small shavings	. 26.272
The same, in thicker shavings	. 25.590
" in thick shavings	. 24.748
" dried in the air	. 29.210
Very dry wood, in thin shavings .	. 29.838
" " thicker do	. 26.227
5. Ash wood.	. 30.666
Common dry wood	. 33.720
The same, dried in air, shavings	
" shavings dried in an oven .	. 35.449
6. Sycamore wood.	
Strongly dried in an oven	. 36.117
7. Wood of Mountain Ash.	
Strongly dried in an oven	. 36.130
Dried brown	. 32.337
8. Wood of Bird Cherry.	00.000
Dried wood	. 33.339
	. 36.904
Dried brown	. 34.736

One Pound of the following kinds of Wood,	Pounds of Water from
when burnt, will heat	32° to 212°.
9. Fir wood (Deal).	
Ordinary dry wood	. 30.332
Well dried in the air, shavings	.34.000
" in an oven, shavings .	. 37.379
" brown in shavings	. 33.358
" in thick shavings	.28.695
10. Poplar wood.	
Wood, dried in the ordinary manner.	. 34.601
" strongly dried in an oven .	. 37.161
11. Hornbeam.	
Dried wood (ordinary)	. 31.704

FUEL.

It was first remarked by Welter that the amount of heat produced by burning bodies is in direct proportion to the quantity of oxygen required to effect their combustion. This circumstance, which was originally deduced from the calorimetrical experiments of Laplace, Rumford, Lavoisier, Despretz, and others, is now generally admitted as an established fact, and has given rise to a new and very convenient method of estimating the calorific value of fuels. The process, invented by Berthier, consists in heating a known weight of the substance in fine powder, with a large excess of litharge, which, being decomposed by the combustible matters of the fuel, yields a button of lead proportionate to the quantity of those substances present. Every atom of oxygen thus abstracted from the litharge will necessarily give rise to the production of an atom of metallic lead, and, consequently, a tolerably accurate measurement of the relative heating values of different kinds of fuel is obtained by weighing the button of lead produced under perfectly similar circumstances by a given weight of each variety. When, however, it is required to ascertain what quantity of water would be elevated from 32° to 212° Fahr. by the combustion of a given amount of any particular fuel, it is found necessary to refer the results to the known calorific value of a single combustible substance. For this purpose, carbon, which, according to Despretz, requires 2.666 times its weight of oxygen for its perfect combustion, is generally chosen. If this be abstracted from litharge entirely free from the higher oxides of lead, each portion of carbon will afford 34.5 parts of metallic lead; and if we further admit, in accordance with the results of the above-mentioned chemist, that the same amount of carbon will elevate 78.15 parts of water from 32° to 212° Fahr., it follows that each amount of lead corresponding to a unity of carbon, which may be reduced by any kind of fuel, corresponds

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to  $\frac{78\cdot15}{34\cdot5}$  = 2.265 parts of water raised by its combustion from 32° to 212°.

The calorific value of a substance may be estimated with still greater accuracy from the results obtained by its ultimate analysis made according to the methods to be hereafter described. As one equiv. of carbon requires 2.666 times its weight of oxygen for its combustion, and an unity of hydrogen takes rather more than triple that quantity, or eight parts, it follows that the amount of oxygen required for the combustion of a substance containing C parts of carbon, H parts of hydrogen, and O parts of oxygen, will be expressed by  $C \times 2.666 \mp (H-h) 8 = x$ , in which h represents the amount of hydrogen corresponding with O parts of oxygen, and must be evidently deducted from the amount contained in the fuel. If, on the contrary, it be required to find the quantity of water which should theoretically be evaporated by a given weight of any particular fuel, of which the ultimate composition is known, the formula becomes  $\frac{C \times 13268 + H - h \times 62470}{C \times 13268 + H - h \times 62470}$ Here C is the quantity of carbon, H the quantity of hydrogen

contained in a unit of fuel, and h the quantity of hydrogen corresponding to the per-centage of oxygen contained in the substance examined. These multiplied by their respective heating powers, according to the experiments of Dulong, and divided by the latent heat of steam, afford the required result.<sup>1</sup>

The calorific values of various kinds of fuel, as calculated by these formulæ, are given in the following tables :---

Species of Wood.	Pounds of Lead reduced by 1 lb. of Wood.	Pounds of Water which 1 lb. of Wood can heat from 32° to 212°.	Wood can eva-	Observers.
Oak wood	12.50	28.30	5.27	Berthier.
Ash	14.96	32.07	5.97	Winkler.
Sycamore	13.10	29.70	5.53	Berthier.
Beech	13.70	31.00	5.77	66
Fir	14.50	32.80	6.11	66
Pine	13.70	31.00	5.77	66
Hornbeam	12.50	28.30	5.27	66
Elm	14.50	32.84	6.12	Winkler.
Poplar .	13.04	29.54	5.50	"
Lime-tree	14.48	32.80	6.11	"

Different kinds of Wood.

<sup>1</sup> The coefficient of the latent heat of steam at 212° Fahr. is generally taken at 1000°. The above number is from the recent experiments of Regnault on this subject.

		eat.

Locality.	Pounds of Lead reduced by 1 lb. of Peat.	Pounds of Water which I lb. of Peat can raise from 32° to 212°.	Pounds of Water which 1 lb. of Peat can evaporate from 212°.	Observers.
Peat from Troyes "Ham, Dép. de la Somme "Bassy, Dép. de la Marne "Königsbrunn, Wirtemberg "Framont, Dép. des Voges "Ischoux, Dép. des Landes From Allan in Ireland, Upper "Lower Pressed Peat 	$\begin{array}{r} 8.0 \\ 12.3 \\ 13.0 \\ 14.3 \\ 15.4 \\ 15.3 \\ 27.7 \\ 25.0 \\ 13.7 \end{array}$	$18.1 \\ 27.9 \\ 29.2 \\ 32.4 \\ 34.9 \\ 34.6 \\ 62.7 \\ 56.6 \\ 28.0$	$ \begin{array}{c} 3:37 \\ 5\cdot2 \\ 5\cdot4 \\ 6\cdot0 \\ 6\cdot5 \\ 6\cdot4 \\ 11\cdot5 \\ 10\cdot5 \\ 5\cdot2 \end{array} $	Berthier. Griffiths.

Brown Coal.

Locality.	Pounds of Lead reduced by l lb. of Coal.	of Coal will heat from 32°	Water which 1 lb. of Coal will evaporate	Observers.
		to 212°.	from 212°.	
Saint Martin de Vaud (Canton de			_	
Vaud)	22.6	15.20	9.54)	
Minerme, Dép. de l'Aude	22.8	51.60	9.61	
Faveau	21.0	47.60	8.87	
Enfant Dort	21.0	47.60	8.87	
Koep Fuarch, Lake of Zurich .	20.7	46.90	3.67	Berthier.
Val, Dép de la Sarthe	19.25	43.60	8.12	
Common German	18.40	41.70	7.77	
Elbogen, Bohemia	18.20	41.20	7.68	
Kumi	15.80	38.80	7.23	
Earthy Coal from Dax	21.38	48.31	9.001	
" Bouches du Rhône	18.89	42.69	7.95	
" Lower Alps .	16.69	37.71	7.02	n I
" Greece	17.84	40.31	7.51	Regnault.
" Cologne	18.24	41.22	7.68	
" Usnach	15.90	35.93	6.69	
Helmstedt, Prinz Wilhelms' Mine	20.17	45.58	8.49)	Varren-
Schöningen	18.76	42.39	7.90}	trapp.

### COMPARATIVE VALUE OF FUELS.

Name of Coal and Locality where is raised.	t is	Pounds of Lead reduced by 1 lb. of Coal.	Pounds of Water which 1 lb. of Coal is capable of elevating from 32° to 212°	Water which 1 lb. of Coal is	Observers.
Aberdare Co.'s Merthyr Hill's Plymouth Works Nixon's Merthyr Thomas's Merthyr Neath Abbey Rock Vawr Blackley Hurst Blackley Hurst Blackbrook Little Delf Laffak Rusby Park	•••••	34·12 34·06 33·20 32·96 31·20 28·92 29·58 28·98 28·68	77:11 76:97 75:53 74:48 70:51 65:35 66:85 65:49 64:81	14·37 14·34 13·98 13·88 13·14 12·18 12·56 12·20 12·08	J. A.
Newcastle Hartley . Carr's Hartley . Hedley's Hartley . Steam-boat Wallsend	• • • • •	26.88 26.88 31.86 30.90 30.36 28.80 28.38	60.74 72.00 69.83 68.61 65.08	12:00 11:32 13:42 13:01 12:78 12:13 11:94	Phillips.
Image: Second state sta	• • • • • • •	29.60 28.1 27.6 27.3 27.0 26.8	54·96 54·96 67·0 63·6 62·5 61·8 61·1 60·7	12·48 11 85 11·65 11·51 11·38 11·31	
Treiul, near St. Etienne St. George's de Lavencas Aveyro Ombrowa, Silesia Salin, Jura Vazas Slavonia Rolduc near Aix-la-Chapelle		25·41 24:0 21·2 21·0 19·4 31·0	57·5 54·5 48·0 47·5 43·9 70·2	10.71 10.15 8.94 8.85 8.18 13.08	Berthier.
Zinsweyer, near Offenberg .	•	22.2	50.3	9.37	

N

Locality.	Pounds of Lead reduced by 1 lb. of Anthracite.	cite will	of Anthra-	Observers.
Lamure, Grenoble Pennsylvania	31.60 30.50	71.50 69.10	13.32 12.88	
Laval la Chaumière	33·0 26·6	74·7 60·2	$  12 00 \\ 13.92 \\ 11.22 $	Berthier.
Corbattrie	26.7	60.5	11.27	TA
Llanguicke, Glamorganshire . Slievardagh, Tipperary	33·48 30·10	75·73 70·44	$\left  \begin{array}{c} 14 \cdot 11 \\ 13 \cdot 12 \end{array} \right\}$	J. A. Phillips.

## Anthracite.

## Charcoal.

Made fr	m	Pounds of Lead reduced by 1 lb. of Charcoal	Pounds of Water which 1 lb. of Charcoal will heat from 32° to 212°	coar will	Observers.
Length of the second se		$\begin{array}{c} 30.6\\ 30.6\\ 29.6\\ 29.5\\ 32.3\\ 32.4\\ 31.4\\ 31.3 \end{array}$	$ \left. \begin{array}{c} \text{On an} \\ \text{average} \\ 68 \end{array} \right. \\ \left. \begin{array}{c} \text{On on} \\ \text{average} \\ 72 \end{array} \right. \end{array} \right. $	12.6	Berthier.
Beech Elm Lime-tree .	· · ·	33·57 33·26 32·79	On an average 75.7	<u> </u>	Winkler.

# Peat Charcoal.

Locality.	Pounds of Lead reduced by 1 lb. of Peat Charcoal.	Water which 1 lb. of Peat	Pounds of Water which 1 lb of Peat Charcoal will evaporate from 2120.	Observers.
Courcy-sur-Ourcq	17.7	40.1	7.47)	
Ham	18.8	40.7	7.77	
Essone	22.4	50.7	9.45	Berthier.
Framont, made from Peat from Champ-de-feu	26.0	58 <b>·9</b>	10.79	

Locality of Coal from which the Coke was made.	Pounds of Lead reduced by 1 lb. of Coke,	Pounds of Water which 1 lb. of Coke will elevate from 32° to 212°.	Pounds of Water which 1 lb. of Coke will evaporate from 212° Fah.	Observers.
St. Etienne, prepared at La Garre	28.5	656	12.2	
Bessèges, Aveyron	28.4	64.3	12.0)	
Rive de Gier	26.0	58.9	10.9	Berthier.
Coke from the Luxembourg gas	1.5 (1.1 (1.1 (1.1 (1.1 (1.1 (1.1 (1.1 (	all realized	(	The state of the
factory, Paris	22.2	503	9.4)	In Million
Tanfield, Durham	31.68	71.59	13.34.	J.A.Phillips.

Coke.

Influence of Time on the Action of Fuels .- The consideration of the actual heating power of different kinds of fuel, without reference to the time necessary for the production of the heat evolved, would afford very superficial and erroneous ideas relative to their respective economic values. If we refer to the foregoing tables, it will be found that the softer and lighter varieties of wood possess higher caloric values than those which are more compact, and have consequently a greater density. This is precisely the reverse of what might be expected from actual experience, but when carefully examined, this apparent anomaly is easily explained. On consulting the table, page 125, showing the ultimate composition of the various kinds of wood, it will be observed that the lighter and more inflammable varieties contain a larger amount of hydrogen than the harder and less combustible kinds. In pure woody fibre, the relative proportions of oxygen and hydrogen are such as by their union would form water, whilst in all the different kinds of wood which have been examined there is a constant excess of the latter over the former. This excess is more considerable in soft woods than in hard. In oak the excess of hydrogen above that necessary to combine with the oxygen amounts to 5.08 parts in 1000, whilst in common deal it amounts to 9.50. When these woods are strongly heated, the excess of hydrogen combines with a portion of the carbon present, and gives rise to the formation of gaseous hydrocarbons, at the expense of the fixed carbon or charcoal, which would otherwise be produced. These gases igniting with extreme readiness, produce much flame, and the woods from which they are evolved consequently consume with greater rapidity than those in which the hydrogen and oxygen exist more nearly in equivalent proportion. When such woods are applied to heating purposes, it is generally found that they evolve their heat more rapidly than the apparatus in which they are consumed is capable of absorbing it, and a considerable

portion is lost, from the circumstance of a certain time being required by all arrangements to appropriate the heat which may be developed by the combustion of the fuel consumed. When, on the contrary, a wood is employed in which the excess of hydrogen is very small, but little flame is produced, and as the combustion goes on slowly, and the heat is produced regularly, the greater proportion of that generated becomes available, and the fuel yields a practical effect superior to those varieties which in reality possess a higher calorific value.

It follows from these considerations, that a fuel which may produce the best effects in an apparatus provided with a large heating surface, may be but ill fitted to be employed in one differently constructed, as each variety requires its own time to evolve the heat which it is capable of developing. For this reason the harder woods are most generally preferred, but when a very intense heat is required, as in the case of the porcelain furnace, it is best obtained by the employment of the softer varieties, it being only necessary that the apparatus be so constructed as to absorb the heat evolved with sufficient rapidity. The results obtained by the use of any given fuel also depend in a great measure on the size of the fragments into which it is divided. If it be thrown on the fire in large pieces, it burns slowly, and a large proportion of the heat generated is absorbed. If it be wood that is employed, and instead of being burnt in the form of large logs, it be first divided into shavings, the combustion will be so rapid that a large portion of the heat will, for all useful purposes, be This arises from the greater facility with which the air lost. comes in contact with it, when in the form of shavings. If, however, the fragments are still further reduced in size, the smallness of the particles, and the close contact existing between them, excludes the entrance of the necessary supply, and for this reason it is extremely difficult to obtain any available heat, either from saw-dust or very finely divided coal.<sup>1</sup>

What has been said chiefly with reference to wood, also applies to the other kinds of fuel, as they are all influenced by their state of division, and the excess of hydrogen which they contain. With regard to pit-coal it has been stated that practically the coke which it produces alone acts as a heating agent, and that the hydrogen, and hydrocarbons generated merely afford by their combustion sufficient heat to counterbalance that absorbed by the escaping gases. The effects obtained will necessarily, in a great degree, depend on the nature of the apparatus in which the fuel

<sup>1</sup> This difficulty is at present in a great degree removed by burning the small coals on a grate so covered with losse lumps of stone as not only to prevent their falling through, but also to spread the supply of air through the interstices of the fuel.

is consumed, but wherever a very high temperature is to be attained in a small space, and considerable pressure is to be borne, coke can with the greatest advantage be employed.

The following Table, from The First Report on Coals suited to the Steam Navy, by Sir H. T. De la Beche, and Dr. Lyon Playfair, shows not only the effects actually produced by several varieties of coal in a well-constructed arrangement, but also those theoretically possible, together with the relation existing between the calorific values of their various constituents.

			1			
	Number of lbs. of	Number	Number	Total num-	Actual	
	Water con-	of lbs, of	of lbs. of	ber of lbs.	number of	
- Destruction	vertible	Water con-	Water con	of Water	lbs. of	Per-cen-
Name or Locality		vertible into	vertible into		Water con-	tage of Coke left
of Coal.	by the	Steam by	Steam by the		verted into	by each
And the set	Coke left by Coal	the carbon of Coal.	hydrogen of Coal.	by 1 lb. of Coal.	Steam by 1 lb. of Coal.	Coal
State and a state	Coal	of Coal	or coal.	Coal	T ID. OF COAL	
AND THE SHOP	Theoretical.	Theoretical.	Theoretical.	Theoretical	Practical.	
Welsh Coals:	Contraction of the second		States Stere	The second second	1	
Graigola	11.301	11.660	1.903	13.563	9.35	85.5
Anthracite (Jones		- talificaters	an This of the	COM PENS	Brn Awring	000
and Aubrey) .	12.554	12.563	2.030	14.593	9.46	92.9
Old Castle Fiery				11000		545
Vein .	10.601	12.046	2.890	14.936	8.94	79.8
Ward's Fiery Vein		12.040	2.542	14.614	9.40	19.8
Binea .					9 94	
	11.560	12.181	2.912	15.093		88.10
Llangennech .	10.599	10.741	2.519	14 260	8'86	83.69
Pentrefellin .	10.841	11.749	2.038	13.787	6.36	85.0
Powell's Duffryn	11.134	12.126	2.966	15.092	10.15	84.3
Mynydd Newydd	9 831	11.463	3.441	14.904	9.52	74.8
Three QuarterRock	a starting the	The second second		NORTH SEALS	THE REPORT	
Vein	7.081	10.325	2.781	13.106	8.84	62.5
Cwm Frood Rock		States States 1	Same and street		and the second	
Vein	8.628	11.300	3.488	14.788	8.70	68.8
Cwm Nanty Gros	8.243	10.767	3.165	13.932	8.42	65.6
Resolven	10.234	10.899	3.072	13.971	9.53	83.9
Pontypool	8.144	11.088	3.207	14.295	7.47	
D.1	8.897	11.075	3.766	14.235	9.79	64.8
Ebbw Vale		12.335	3.300			71.7
	10.441	12.999	3'300	15.635	10.21	77.5
Porthmawr Rock		10.000				
Vein	6.647	10.263	2.548	12.811	7.53	63.1
Coleshill	6.468	10.145	2.654	12.799	8.00	56.0
Scotch Coals:	and Arman	ratif etstation	Article Article	hi at heat	a setting	
Dalkeith Jewel	- A BARRA	a standard and	A ALANDARY	and a wint ?	- Salar In	
Seam	6.239	10 242	2.071	12.313	7.08	49.8
Dalkeith Corona-	1.	Statistics and	ALC: NOT	月中 (1)(1)	and the second second	14 1 1 S. A.
tion Seam	6.924	10.570	2.202	12.772	7.71	53.5
Elgin Wallsend .	6.560	10.454	2.968	13.422	8.46	58.45
Fordel Splint	6.560	10.933	2.884	13.817	7.56	52.03
0 1	7.292	10.970	2.722	13.692	7.40	56.6
English:	1 202	20010	4124	10 002	1 10	0.00
Bromhill	7.711	11.225	3.638	14.969	7.30	50.0
	111	11-220	9.099	14.863	1.90	59.2
Irish:	a contraction	CH MARY	CARGE STREET		Star Car	19 19 19
Slievardagh (an-		10.005		10.100		
thracite) .	10.895	10.995	1.487	12.482	9.85	90.1
and the second second second		Sall Constants			1	111111

# OF THE VARIOUS METHODS FOR ASCERTAINING THE RELATIVE VALUE OF FUELS.

Those fuels which possess the highest calorific powers are not always such as should be invariably selected for practical purposes, as they may nevertheless be subject to disadvantages which more than counterbalance this property. It is therefore necessary to ascertain, by experiment, what are the peculiar characteristics of each variety, so as to be enabled to select from among a number such as may be most economically employed for the particular purpose to which the fuel is to be applied.

**Estimation of Ash.**—If the substance to be examined be a wood, it should be first reduced to fine powder, by means of a rasp, or if it be friable, such as charcoal, pit-coal, or coke, it may be pounded in an iron mortar.

A weighed portion (about 10 grains) of the pulverised fuel is then placed either in a platinum or porcelain crucible and ignited over a gas flame, until the whole of the combustible matter is consumed. The residue is subsequently weighed, and from the amount left the per-centage of incombustible matter present is estimated. In making this experiment, much time will be saved by placing the crucible a little on one side, and partially covering its mouth with the lid for the purpose of directing a current of air on the burning body. When the substance to be examined is a caking coal, it is found advantageous not to break the crust of coke which is first formed, but to allow the mass gradually to consume from the exterior. If this be not attended to, and it should contain much ash, small portions are frequently protected by a coating of earthy matters, and escape complete combustion. In the case of coke it is sometimes found extremely difficult to consume the last portions of carbon, but this may always be effected either by roasting the substance in an assay muffle, or by subjecting it, at a red heat, to the action of oxygen gas.

The latter process is best accomplished by placing a known weight of pulverised coke in a porcelain crucible over a lamp, and when from the accumulation of ash the combustion becomes sluggish, the vessel is closed by a cover having a hole through its centre, and by this a current of oxygen is made to arrive through a suitable tube from a gas-holder in which it is contained. The amount employed is regulated by a stop-cock, and too rapid action is especially to be avoided.

**Estimation of Hygrometric Water.** — The amount of water present is estimated by drying a known quantity of the substance in a water or air bath, heated to 212° Fah., until it ceases to lose weight. In accurate determinations, all experiments should at least be repeated twice, as perfect reliance can never be placed in results when this precaution has not been attended to.

**Sulphur**.—The sulphur contained in a fuel is most correctly determined by the following process. The substance to be examined is intimately mixed with twice its weight of pure carbonate of magnesia, and placed in a bulb blown in the middle of a tube made of hard glass. This is strongly heated either by a spirit-lamp or gas-flame, at the same time that a continuous current of oxygen gas is passed through it from an apparatus attached for that purpose. When the whole of the carbonaceous matter is completely consumed, which is easily perceived by the whiteness of the mixture, the powder is thrown on a filter, and the soluble sulphate of magnesia washed through, whilst the insoluble carbonate remains behind.

The sulphuric acid in the filtrate is then thrown down by chloride of barium, and from the weight of sulphate of baryta obtained, the per-centage amount of sulphur present in the original substance is deduced.

Carbonate of lime may for this purpose be employed, instead of the corresponding salt of magnesia, but as the sulphate of lime is less soluble than sulphate of magnesia, the washing on the filter requires to be prolonged, and a longer time is necessary for the completion of the operation than for that above described.

The sulphur may also be more rapidly, but perhaps less correctly estimated by igniting in a platinum crucible a mixture of the substance to be examined with three times its weight of nitre and four times that quantity of pure carbonate of soda. When this method is employed, the fused mass which remains in the crucible is first dissolved in water, and after being filtered is rendered acid by the addition of either nitric or hydrochloric acid. The filtrate is then treated with a sufficient amount of chloride of barium as above described.

**Carbon and Hydrogen.**—These constituents are usually estimated according to the methods employed for the analysis of organic substances; but the best results are always obtained when a quantity of matter not exceeding five grains is operated on. Experience also shows that the combustion of fuels is more completely effected by the use of oxide of copper than when chromate . of lead is employed, and that whenever the substance burns with difficulty, as in the case of coal, and more particularly of anthracite, it is necessary, not only to use a long combustion-tube, but also a certain portion of dry chlorate of potash, which, after being mixed with oxide of copper, is placed at the sealed end of the tube so as to give off pure oxygen gas towards the close of the operation. Nitrogen.—The amount of nitrogen contained in a fuel cannot be considered of much practical importance, and it may therefore, in most instances, be included with the oxygen : if necessary, however, it can be easily estimated by the method of Will and Varrentrapp.<sup>1</sup>

**Oxygen**.—This element is invariably estimated by the loss on analysis.

Litharge Experiments.—In most instances, the calorific value of fuels may be ascertained with sufficient accuracy without having recourse to an accurate analytical examination, and for this purpose the process employed by Berthier is the most simple, and, at the same time, one of the most accurate.

The weight of substance operated on may be about five grains, and the greatest care should be taken to obtain it in the finest possible state of division. If the substance be brittle, such as coal, coke, or charcoal, it is easily pounded in a mortar, and afterwards sifted; but if it be a variety of wood which is to be experimented on, the saw-dust obtained by cutting it with a fine saw, or scratching with a file, should be employed. This should, according to its supposed richness, be intimately mixed with from 150 to 250 grains of litharge, and placed in a small earthen assay crucible. On this is placed from 100 to 150 grains of pure litharge, and after the whole has been shaken down, the crucible ought not to be more than half full, in order to allow sufficient space for the intumescence of the mixture when in a semi-fluid state. The crucible is now stopped by a cover, which is carefully luted with fire-clay for the purpose of preventing any fragments of coke or reducing gases from the fire from vitiating the result, and the whole is placed in an assay furnace already lighted, and in which there is a tolerable supply of hot coke. Here it is gently heated during about fifteen or twenty minutes, at the expiration of which time the contents will be in a state of tranquil fusion. The crucible is now to be covered with hot coke, and the draught increased by means of the damper, in order to cause the whole of the reduced lead to collect in the form of a button at the bottom. Care should likewise be taken to prevent any loss of metal by volatilisation, and a moderate temperature only should consequently be employed. This will usually be effected in about ten minutes, and the crucible is then withdrawn from the fire and slightly tapped against some hard body, to throw down any globules which might remain suspended in the fused litharge. After being allowed to get cold, the crucible is broken and the button

<sup>1</sup> For directions relative to the analysis of organic substances, see "Instructions in Quantitative Chemical Analysis," by Dr. C. R. Fresenius, p. 392, &c. of lead extracted, and from its weight is calculated the calorific value of the fuel according to the data given at page 175. If the operation has been properly conducted, the button of lead separates easily both from the crucible and the melted litharge by which it is surrounded; but in case of anything adhering to it, its removal is readily effected by first hammering the button on an anvil, and afterwards brushing off the small particles sticking to it with a hard brush. The results thus obtained from different experiments on the same substance will be found to agree very closely with each other. But on comparing the calorific value of a fuel as obtained by the litharge process, with that calculated from its ultimate analysis, the former is found to afford about one-ninth less than those obtained by the latter method. This process, therefore, although not admitting of absolute accuracy, is sufficiently exact for many practical purposes.

The exactitude of such determinations is sometimes also slightly influenced by the presence of iron pyrites and protosulphide of iron, both of which exercise the same reducing influence on the litharge as that produced by the combustibles themselves. When heated with reducing agents, the sulphur of these substances escapes in the form of sulphurous acid, whilst the iron with which it was combined remains with the litharge in the state of protoxide.

These reactions determine the reduction of a certain quantity of metallic lead which interferes with the experiment, and, to a certain degree, vitiates the result.

Allowance for this source of error is, however, easily made when the quantity of sulphur present has been previously determined; for since 100 parts of pyrites is capable of reducing to the metallic state 840 parts of lead, and the same amount of the protosulphide will reduce 720 parts of that metal, we have sufficient data from which to calculate the quantity of metal due to these impurities; and this must evidently be deducted from the total amount obtained by the experiment.<sup>1</sup>

<sup>1</sup> The sulphur contained in coal, lignite, and other fuels, which have not been subjected to a strong heat, appears invariably to occur in the form of iron pyrites, whilst that which is found in coke and other charred fuels is reduced to the state of protosulphide of iron. When any doubt exists as to the state in which the sulphur occurs, the question is easily decided by adding a few drops of hydrochloric acid to a little of the powdered fuel: if sulphuretted hydrogen be evolved, it is a proof of the presence of the protosulphide, whilst the reverse shows that the sulphur which it contains does not occur in that form.

## FURNACE MATERIALS.

THE refractory lining of furnaces is usually composed of bricks prepared from various compounds known by the name of fireclays; although less frequently, and particularly for the internal casing of the hearths of iron furnaces, certain siliceous sandstones are sometimes employed.

Clays are essentially composed of silica, alumina, and water, but are almost invariably more or less mixed with other bodies, by the presence of which their properties are considerably modified. Pure clays are white, opaque, and unctuous to the touch; when dried, they present an earthy fracture, and if placed on the tongue, give rise to a peculiar sensation of dryness. When put into water, these compounds have the property of swelling up and becoming suspended in that liquid, and thus afford ductile tenacious pastes, readily admitting of being moulded into any required form. Bv calcination at an elevated temperature, the water is gradually expelled, and considerable contraction of the mass takes place. When free from all admixture with other bodies, clays are infusible at the highest temperature to be obtained in our furnaces, but they sometimes, when thus treated, become so far softened that crucibles formed of this material bend, and become much deformed under the pressure of the tongs, by the aid of which they are withdrawn from the fire. The lustrous aspect frequently observed on breaking a pot which has been very highly heated is also an indication that incipient fusion had commenced, and is in this respect analogous to the appearances observed in some kinds of pottery, on which the glazing has been applied at a very elevated temperature.

It was formerly supposed that clays were mere admixtures of silica, alumina, and other bodies arising from the gradual disintegration of the rocks in the vicinity of the localities in which they are produced: but it is now universally admitted that they are definite chemical compounds of silica, alumina, and water, and that the various other bodies with which they are found associated are mere mechanical mixtures, which should only be regarded as impurities. The bodies found accompanying clays, and in a state of intimate mechanical mixture with them, are extremely numerous; but among the most common of these impurities may be mentioned oxide of iron, carbonate of lime, iron pyrites, graphite, and various bituminous matters. The presence of these substances materially impairs the quality of the clays in which they are found, as, by combining with a portion of the silica present, a series of fusible vitreous compounds are produced. The degree of heat necessary to effect the fusion of these substances is not entirely dependent on the amount of basic matter thus brought in contact with the natural silicate, but is also in a remarkable manner influenced by the nature and number of the bases themselves.

In this way a clay containing a given amount of lime is found to be less fusible than another similarly constituted, except that a certain portion of the lime is replaced by an equivalent amount of magnesia; and if three or more bases be present instead of one, the compound will be found proportionately more easy of fusion. Among the purer varieties of clay, the most refractory are those in which the proportion of silica is greatest; and reaches its maximum in those substances which, although exhibiting many of the physical properties of clays, can scarcely be classified among them on account of their very large per-centage of silica : such, for example, are the different varieties consisting of the siliceous remains of infusoria, commonly known by the name of rottenstone.

Clays, in their natural state, are seldom capable of fulfilling the whole of the several conditions which may be required of them, and it therefore becomes necessary to make such additions as an accurate analysis, and a careful comparison of the results with those obtained from other refractory materials, may suggest. Attention to this subject becomes the more important from the circumstance that many varieties of clay which possess the requisite degree of infusibility are, when subjected to a rapidly increasing change of temperature, liable to split and fly, from the too great expansion or contraction of the mass. The chief additions made in this case consist of pure siliceous sand, and ground and previously burnt fire-clay, which, without increasing the fusibility of the compound, has the property of rendering the baked material less liable to become broken through the too rapid application of heat.

The examination of seven varieties of fire-clay from the neighbourhood of Newcastle-on-Tyne, where an extensive trade is carried on in fire-bricks and clay gas-retorts, afforded Dr. Richardson the following results :—(See next page.)

The manufacture of refractory bricks is conducted in a precisely similar way to that of those employed for ordinary building purposes.

The fire-clay, after being some time exposed to the air, is

	1	2	3	4	5	6	7
Silica Alumina Oxide of Iron . Lime Magnesia Water and Organic Matter	$51.10 \\ 31.35 \\ 4.63 \\ 1.46 \\ 1.54 \\ 10.47$	47.55 29.50 9.13 1.34 0.71 12.01	48.55 30.25 4.06 1.66 1.91 10.67	51.11 30.40 4.91 1.76 Trace 12.29	71·28 17·75 } 2·43 2·30 6·94	$\begin{array}{c} 83 \cdot 29 \\ 8 \cdot 10 \\ 1 \cdot 88 \\ 2 \cdot 99 \\ 3 \cdot 64 \end{array}$	$\left.\begin{array}{c} 69 \cdot 25 \\ 17 \cdot 90 \\ 2 \cdot 97 \\ \end{array}\right\} 1 \cdot 30 \\ 7 \cdot 58 \end{array}$

crushed under a pair of heavy edge-stones, where it is ground together with a mixture of previously-baked clay of the same description, until it has been reduced to the state of coarse powder. This falls through a hole in the bedstone, and is from thence mounted by the buckets of an endless chain into a large cylindrical sieve, by which it is divided into two classes. The coarser fragments which remain on the meshes are returned under the edgerunners, to be again ground, whilst the finer particles which have passed through the apertures are conducted by an endless belt to a convenient situation, where it is deposited under a continuous stream of water. The mixture is subsequently incorporated in a pug-mill, and moulded into fire-bricks in the way adopted for the more common varieties employed for building purposes. A man and boy may in this way with a hand-mould make and lay out to dry 1500 bricks in the course of an ordinary day's work. When sufficiently dried in the sun, they are baked during five days in kilns containing from 15,000 to 20,000. A ton of coal is, on an average, required for the baking of every 3,000 bricks, which are all placed lengthways, and separated from each other by about a finger's breadth in order to allow a free passage between them of the heated gases produced by the combustion of the fuel, the whole of which is consumed at the extremity of the pile furthest removed from the chimney.

**Crucibles** are commonly manufactured either by working the prepared clay on a potter's wheel, similar to that employed in making ordinary pottery, or by compressing the prepared clay in strong bronze moulds, which thus communicates to the mass the required form. Sometimes, also, although more rarely, crucibles are prepared by covering with the hand a mandril made either of metal or hard wood, and having the exact form and dimensions of the internal cavity of the vessel required. To be perfect in every respect, they should, in the first place, be capable of resisting without fracture the most sudden changes of temperature.

They should also be infusible, be unacted on by the substances which are to be fused in them, and lastly, be impermeable to both liquids and gases. It would, however, be impossible to prepare vessels capable of fulfilling all these conditions, and consequently it is generally found more convenient to select the mixture to be employed in accordance to the uses to which it is to be applied, than to attempt the manufacture of pots which shall be applicable to every sort of use.

When it is desired to prepare crucibles capable of withstanding very sudden changes of temperature, the prepared clay is intimately mixed with various infusible bodies which are not liable to expand on being strongly heated. These substances are called cements, and generally consist of siliceous sand, ground flints, calcined clay, graphite, or finely-powdered coke.

The most infusible crucibles are prepared from clays containing the largest proportion of silica, and in which the amount of lime and oxide of iron is extremely minute. The infusibility of clay, like its power of sustaining sudden changes of temperature, may be much increased by a judicious admixture of cement, which, from forming a kind of infusible ground-work, prevents the crucible from being deformed by exposure to a temperature by which it would be otherwise destroyed. The most efficient cement for the purpose is graphite or finely-powdered coke added to the clay in the proportion of about one-third, since, if a larger amount were used, although the infusibility of the crucible might to a certain extent be increased, the carbonaceous matters are liable to become consumed by repeated use, and the crucible is by this means gradually destroyed.

The composition of some of the best varieties of fire-clay, as deduced from the experiments of Berthier and Salvetat, is given in the following table :—<sup>1</sup>

Dried at 212°.	Gross Almerode.		Beaufays, Dep. des Ardennes.	ne	ey Hill, ear oridge.	Schierdorf, near Passau.	
	Berthier.	Salvetat.	Berthier.	Berthier.	Salvetat.	Salvetat.	
Hygrometric Water } Combined Water Silica Alumina Oxide of Iron . Lime	15·2 46·5 34·9 3·0	0.43 14.00 47.50 34.37 1.24 0.50	19·0 52·0 27·0 2·0	10·3 63·7 20·7 4·0	17·34 45·25 28·77 7·72 0·47	0.50 16.50 45.79 28.10 6.55 2.00	
Magnesia Alkalies	6 -07-C -0	1.00 Trace.	10000				

<sup>1</sup> Knapp's Technology, vol. ii. p. 355.

#### FURNACE MATERIALS.

The composition of several different kinds of manufactured crucibles has been carefully examined by Berthier, whose results are arranged in the following tabular form :----

Place of Manufacture.	Silica.	Alumina.	Oxide of Iron.	Mag- nesia.
Crucibles from Gross Almerode	70.964.672.361.065.267.468.0	$ \begin{array}{r} 24.8 \\ 34.4 \\ 19.5 \\ 23.0 \\ 25.0 \\ 32.0 \\ 29.0 \\ \end{array} $	$   \begin{array}{r}     3.8 \\     1.0 \\     3.9 \\     4.0 \\     7.2 \\     0.8 \\     2.2   \end{array} $	  0·5

In order that a crucible be but slightly attacked by the bodies fused in it, it is not only necessary that the particles of which it is composed should be finely divided and closely compressed, but also that it should have but little affinity for the substance operated on.

The metals, together with their compounds, with the exception of the oxides, exert little action on crucibles made of ordinary fireclay, although galena, together with some other substances, has the property of filtering through the pores of earthen crucibles without exercising on their constituents any apparent chemical action. The degree of facility with which clay pots yield to the action of metallic oxides is usually tested by the fusion of litharge, which is maintained in the fluid state until the pot becomes pierced by its corroding action on its sides, when the time necessary to produce this effect is noted and compared with similar results obtained with other varieties of crucibles.

The degree of fusibility of crucibles and other refractory bodies is best ascertained by a direct experiment conducted in the following manner :—A piece of the substance to be examined, and which for this purpose should present numerous sharp edges, is heated in a refractory crucible lined with powdered charcoal to the fullest extent possible in a large wind furnace. The pot and its contents are then allowed to cool, and on afterwards breaking it and slowly examining its contents, it will be observed whether or not the thin edges of the broken fragment have become rounded or rendered translucent, in which case it affords a sufficient indication that a commencement of fusion has taken place.

The permeability of crucibles by liquids is best determined by filling them with water, and noting what time respectively elapses

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with each variety before any appearance of dampness can be perceived on the outside.

For the purpose of ascertaining their power of resisting sudden changes of temperature, crucibles may be thrown, without any previous annealing, into an intensely-heated furnace and afterwards withdrawn and at once exposed to a current of cold air.

Three different kinds of crucibles are used by assayers in this country, viz., the Hessian, the London, and the Cornish; and of these the two latter are the most extensively employed.

The shape of the Cornish pots is generally inconvenient, from their great flatness at the bottom, but in all cases where great heats are to be employed, and sudden changes of temperatures to be undergone, they are to be preferred to every other variety, excepting those manufactured at Beaufays.

The stones in various localities employed for furnace bottoms are chiefly siliceous sandstones from the coal formations, free from lime, and containing but small quantities of oxide of iron.

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# IRON.

# Equiv. = 28. Density, = 7.8.

IRON is a metal of a bluish-grey colour and fibrous fracture, but is easily made, by polishing, to acquire a brilliant surface. It possesses greater tenacity than any known metal, and is at the same time the hardest of those which are malleable and ductile. The iron of commerce is not, however, chemically pure; for, besides containing variable qualities of carbon, traces of silicium, sulphur, and phosphorus, may invariably be detected. The presence of these substances materially influences the quality of the metal, and therefore for objects requiring great nicety of construction the purest varieties are alone employed.

These impurities may be removed from iron by the following process. Some fine iron wire is first cut into short pieces, and then partially oxidised either by heating it, with exposure to the air, or, which is still better, by passing the vapour of water over it at a red heat in a porcelain tube. This, on being withdrawn from the tube, is mixed with a small quantity of pulverised hard glass and placed in a porcelain crucible.

The crucible is then enclosed in an earthen one, to which a cover has been luted with fire-clay, and the whole is placed in a furnace, where it is subjected to an intense white heat. By this treatment, the small quantities of foreign matter which occur in the metal are oxidised at the expense of the oxide of iron, whilst the excess of the latter, together with whatever amount of silica may have been produced, will combine with the vitreous flux and form a slag. If the operation be properly conducted, a button of metal will be found at the bottom of the crucible, to which it generally adheres, and which must be broken in order to detach it. The iron thus obtained is of a whiter colour, and more malleable, than that met with in commerce, but possesses less tenacity and ductility than before its purification.

Pure metallic iron is also to be obtained by passing a current of hydrogen gas over one of its oxides heated to a proper temperature in a porcelain or hard-glass tube. This reduction takes place at a low red heat, but as the metal produced will in this case remain in a spongy state, and therefore very readily absorb oxygen, it becomes necessary to keep it entirely from contact with the air, for which purpose the two ends of the tube are either closely corked, or closed before the blowpipe when still full of hydrogen gas. The iron so obtained has the property of absorbing oxygen with such extreme rapidity as to cause the ignition of the whole mass on the removal of the corks, and is thereby converted into sesquioxide. When, however, the experiment has been made at a more elevated temperature, the reduced iron no longer possesses this property, and may be freely exposed without danger of ignition.

When, instead of oxide of iron, the protochloride is thus treated, the reduced metal adheres to the sides of the reduction-tube in the form of a brilliant metallic coating, on which well-defined cubical crystals of metal are frequently perceived.

The texture of commercial iron varies according to the nature of the processes to which it has been subjected during its preparation. A piece of iron which has been equally hammered in every direction will, on being broken, be found to have a finely granular structure; but when it has been drawn into long bars, in which form it usually comes into the market, the texture will be invariably more or less fibrous in the direction of their length. This silkiness of appearance is most distinct in the better varieties of iron, and its structure is therefore one of the best indices of the quality of the metal. By skilful management this peculiarity may, however, be in a certain degree imparted to the commoner varieties, and it is, consequently, unsafe from this circumstance alone to judge of the value of iron. It is also found that the most fibrous varieties do not retain their peculiarity of structure for an indefinite time, but that after a certain period the grain of the metal often assumes a crystalline appearance. These changes are most frequently observed to take place in the tension-rods of suspension-bridges, and in other situations where the metal is subject to constant vibrations. The same effect is also produced by friction, and for that reason the axles of locomotives and railway waggons are often found to acquire a crystalline structure, and are thereby rendered harder and more brittle than the metal from which they were originally made.

In order to melt this metal, the strongest heat of a wind furnace is required; but when combined with a small proportion of carbon its fusion is more readily effected.

On cooling melted iron, it assumes a pasty consistence before taking the solid form, and it is therefore extremely difficult to obtain it in a crystallised state. When, however, large masses are allowed to cool very slowly, as sometimes happens in the case of the heavy girders which support the sides of furnaces, distinct indications of a cubical crystallisation are obtained. At a full red

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heat iron may be hammered into any required form, and on being heated to whiteness, two fragments may be firmly joined together without the aid of any kind of solder. This operation, which is called *welding*, is effected by heating two pieces of metal until the exterior is in a semi-liquid state, and then quickly uniting them by repeated blows from a heavy hammer. Considerable experience is requisite in order to effect this object; for on heating iron to the requisite temperature, it becomes externally coated with a layer of oxide, which would effectually prevent the union of the two fragments if not previously removed.

To prevent the formation of much oxide, as well as to combine with that unavoidably produced, a little siliceous sand is often sprinkled on the ends of pieces which are to be united before they are placed in the fire. This has not only the effect of combining with any portions of oxide that may be formed, and thereby removing it from the surface of the metal, but the silicate of iron thus produced forms a kind of varnish, which effectually preserves it from any further action of the air.

On withdrawing the bars from the fire, this is, by a rapid motion of the mass, shaken off, and two perfectly clean metallic surfaces are thus brought in contact.

Iron and nickel are the only metals which are magnetic at ordinary temperatures. If a mass of iron be either brought in contact with, or placed at a short distance from a natural or artificial magnet, it becomes itself magnetic, but loses this property the instant the exciting magnet is removed. When iron is combined with a certain amount of carbon, it is known by the name of steel. This substance is much less susceptible of the magnetic influence than ordinary iron, but when once the power has been communicated, it is retained for a considerable time after the removal of the magnet from which it was acquired. Permanent magnets may be obtained by rubbing a bar of steel either with a loadstone or an artificial magnet, and in this way an infinite number of steel bars may be rendered magnetic without at all diminishing the power of the bar by which the effect has been produced. The magnetic power of iron is much influenced by its temperature, as the magnetic needle is but little affected by a mass of that metal when made red hot, but in cooling it will be found to gradually regain its magnetic properties.

Iron may be indefinitely exposed to the action of dry air, or even of dry oxygen gas, without becoming oxidised; but if the air or gas contain any portion of watery vapour, the surface of the metal quickly becomes coated with a layer of *rust*. This is produced by the oxidation of the surface of the metal when exposed in a moist atmosphere. The formation of oxide is also much accelerated by the presence of carbonic acid, of which a certain portion is always present in the air; for under the influence of this acid and oxygen, a carbonate of the protoxide of iron is quickly produced. This soon absorbs a further amount of moisture and oxygen from the air, and is thereby converted into hydrated peroxide, whilst the carbonic acid which is evolved facilitates the oxidation of a further portion of metallic iron. When a spot of rust has made its appearance on a piece of this metal, the oxidation of the remaining portions is found to be materially affected by its presence, for the coating of peroxide formed, being electro-negative with regard to the metallic iron which is beneath it, gives rise to a galvanic action, by which the metal is rendered positive. This electric condition of the metal so far increases its affinity for oxygen as to enable it to decompose water at ordinary temperatures with the formation of a further amount of oxide and the evolution of hydrogen in the gaseous form. Oxide of iron thus obtained by exposure to the air usually contains small quantities of ammonia, the presence of which in iron rust may be explained as follows :- The water, by the aid of which the oxidation is effected, contains in solution a certain amount of air, and consequently of nitrogen gas, which, by uniting with the hydrogen produced by the decomposition of water, leads to the formation of this substance.

The formation of ammonia in ordinary rust of iron must be considered as an important fact, since it was formerly supposed that its presence could only arise from the decomposition of animal matter. Whenever, therefore, ammonia was discovered in rust covering the blade of any cutting instrument with which a crime was supposed to have been committed, it was considered as a sure indication that the marks produced were the effect of spots of blood remaining on the weapon.'

This supposition is, however, entirely erroneous, as we have just seen that rust caused merely by exposure to a damp atmosphere, in most instances contains traces of this substance.

When iron is strongly heated and exposed to the air, its surface is quickly covered with a coating of black oxide, which, on being struck with a hammer, easily scales off. It is this property of iron which causes it to afford sparks when struck with a flint or other hard body. Under these circumstances, small particles of iron are torn off by the flint, which produces sufficient heat by friction to render the particles of the metal incandescent on

<sup>1</sup> The presence of ammonia may be detected by heating a portion of the rust with caustic potash in a test-tube, when the characteristic odour of the volatile alkali will be at once perceived.

combining with the oxygen of the air, and by allowing these heated particles to fall on any easily ignitable substance, such as tinder or amadou, a fire is easily obtained. If, instead of tinder, a piece of paper be held beneath the metal during the time it is being struck by the flint, its surface soon becomes covered with small fragments of black oxide of iron, fused into minute globules, and readily attracted by the magnet.

Iron is attacked by hydrochloric acid with the formation of protochloride, and the evolution of hydrogen gas. By weak sulphuric acid it is dissolved even in the cold, hydrogen gas being at the same time given off. Concentrated sulphuric acid also attacks and dissolves iron, but in this case the oxygen is supplied to the metal at the expense of the acid, and sulphurous acid is evolved. Nitric acid attacks it with the evolution of abundant nitrous vapours; but if the acid be very dilute the iron is dissolved without any apparent escape of gas, nitrate of protoxide of iron, and nitrate of ammonia, being produced.

For the purposes of the arts, iron is invariably obtained from the native carbonates and oxides of that metal, which, together with various less important ores, will be hereafter described.

Native Iron.—The existence of this metal in a native state was for a long time a matter of dispute among mineralogists; but it is now generally admitted that, although of rare occurrence, specimens of native malleable iron have been occasionally discovered.

At the mines of Kamsdorf and Eibestock, in Saxony, Karsten and Lehman found native iron forming the centres of stalactiform masses of brown hematite. The same phenomenon has also been observed in the mountains of Oulle, near Grenoble, by Schreiber, who adds that the vein which traverses Gneiss, had not been anciently worked, and that consequently there could be no possibility of the metal having been at a remote period placed in the mine by human agency. The lode in which this native iron occurs possesses no other remarkable peculiarity, and in no part affords the slightest evidence of having at any time experienced a high temperature. From the appearance of specimens of the iron from Kamsdorf, which are in the collections of the Jardin des Plantes and Ecole des Mines of Paris, it would appear that these metallic kernels have been produced by the decomposition of a portion of the oxide in which they are imbedded; but in what way this change could have been effected is difficult to understand, although it is well known that somewhat similar transformations are occasionally produced by electro-chemical agency.<sup>1</sup> This native metal is not,

The most reasonable method of explaining this change appears to be by

however, exactly like ordinary malleable iron, but is whiter, more ductile, and somewhat less dense than that artificially obtained.

**Steely Iron.**—Native iron is also sometimes formed by the spontaneous ignition of seams of coal in the immediate vicinity of ferruginous deposits. The fragments thus produced occur in the form of small button ingots with a finely striated surface, and are usually known by the name of *native steel*. They are excessively hard and fine-grained, and when broken, present a fracture resembling that of ordinary cast steel. A mass of this substance, weighing 16 lbs. 6 oz., was discovered some years since by M. Mossier, at Labouiche, near Nery, in the department of the Allier, where a burning seam of coal had formerly existed.

**Meteoric Iron.**—Large masses of metallic iron are occasionally discovered on the surface of the soil in different parts of the globe, whilst others of similar appearance have from time to time been observed to fall from the atmosphere in the meteoric form.

These meteorites are easily distinguished from the masses of terrestrial iron before described, both by their structure and composition, as they not only invariably contain a greater or less proportion of nickel, which never occurs in the ores of iron, but the metal itself is usually found in the form of a network enclosing crystals of a substance in appearance resembling peridot, but which is soluble in acids. Meteoric iron is always covered on the surface with a sort of black siliceous varnish, which effectually protects the exterior from the rusting action of the atmosphere, although, when this is removed, the metal is as easily oxidised as common iron. Above twenty different masses supposed to be of meteoric origin have been enumerated as existing in various parts of the world, and have in some instances furnished the inhabitants of the countries in which they are found with the materials for making knives, spears, and other instruments. Among the most remarkable is that discovered by Pallas in Siberia, which originally weighed about 1600 lbs.; that of Bahia, in Brazil, weighing 14,000 lbs.; that discovered by Don Rubin de Celis in the district of Chaco-Gualamba, in South America, weighing 30,000 lbs.; that of Elbogen, in Bohemia, which weighed 120 lbs., and that of Agram, in Croatia, which fell from the sky in 1750 in the presence of many witnesses. Two large masses of native iron are also mentioned by Captain Ross as occurring in Greenland, and

supposing that the whole or a portion of the iron formerly existed in the form of iron pyrites (bisulphide of iron), which, becoming oxidised, not only produced a certain amount of the soluble sulphate of iron, but also generated by chemical action an electric current of sufficient power to precipitate a part of the iron in the metallic form.

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several others have been found in Africa, as well as on the continent of North America.

The composition of six different specimens of meteoric iron are given below.

	Iron f <mark>ro</mark> m Siberia.	Iron from Agram.	Iron from Elbogen.	Iron from Santa Rosa.	Iron from Louisiana	
	Klaproth.	Klaproth.	John.	Boussingault.	Shepard.	Turner.
Iron Nickel Cobalt	98.60 1.20 0.00	96·50 3·50 0·00	$91.25 \\ 8.70 \\ 0.00$	91·40 8 59 0·00	90·02 9·61 0·00	93·40 6·62 0·53

Besides these masses of metallic iron, numerous aerolites, containing other substances in addition to that metal, have at different times fallen from the atmosphere. The following table shows the per-centage composition of several of these bodies which have been examined by various chemists :---

	1.	2.	3.	<b>4.</b>	5.	6.
Silica	 48.25	38.06	46.00	30.13	33.90	43.00
Alumina	 14.50	3.47	6.00	3.82		
Magnesia	 2.00	29.93	1.60	38.13	32.00	22.00
Lime	 9.50		7.50	0.14		0.50
Oxide of Iron .	 	4.90	36.00	29.44	31.00	
" Manganese	 	1.15	2.80	Trace		0.25
Potash	 			0.27		
Soda	 			0.86		
Sulphur	2.75	2.70	1.50	0.39		3.50
Iron	23.00	17.49		7.70		29.00
Nickel .	Trace	1.36		1.55		
Chromium .			1.00		2.00	0.50

1. A stone which fell at Stannern, in Moravia, on the 22d of May, 1808. Analysed by Klaproth.

2. A stone which fell at Kostritz, in Russia, on the 13th of October, 1820. Analysed by Stromeyer.

3. Analysis of a stone which fell at Jouzac, on the 13th of June, 1819. By Laugier.

4. Analysis of a stone which fell at Château Renard, on the 12th of June, 1841. By Dufrénoy.

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5. Shows the composition of a stone which fell at Chassigny, near Langres, on the 3d of October, 1815. Analysed by Vauquelin.

6. A stone which fell at Lissa, in Bohemia, on the 3d of September, 1808. Analysed by Klaproth.

#### ORES OF IRON.

No other metal is so universally diffused as iron. It not only exists in a vast variety of minerals as forming one of their essential ingredients, but is so constantly present as an adventitious mixture in all mineral substances, that the chemist seldom makes the analysis of an inorganic body without detecting a certain portion of this metal. As a constituent of organised bodies it is also extremely common, and is, in various forms, present in all animals as well as in the greater proportion of vegetable structures.

A detailed description of the various ores of iron would require much more space than is consistent with the limits of the present work; and for this reason such only will be noticed as are most extensively applied to the purposes of the arts.

Magnetic Iron Ore; Fer oxydulé; Magneteisenstein.—This substance, of which the primitive form is a cube, often occurs in octahedrons and dodecahedrons.

It possesses a cleavage which is frequently distinctly parallel to the faces of the octahedron. It is brittle, of an iron-black colour, and leaves a black streak.

This ore has a density which varies from 5.0 to 5.1, is strongly attracted by the magnet, and sometimes possesses an independent polarity.

Its chemical composition is as follows :---

Iron .		. 71.7	8]	(Perox	ide of Iron	. 69.
Oxygen		. 28.2	$2 \int 0$	Proto:	ide of Iron xide .	. 31.
Corres	spondi	ng to t			or Fe <sub>0</sub> O <sub>4</sub> +H	

Magnetic iron occurs in granite, gneiss, mica-slate, clay-slate, syenite, hornblende, and chlorite, as also less frequently in limestone formations. No ore of iron is more universally diffused than this oxide, which is inferior to none for the manufacture of iron. Nearly all the Swedish iron is obtained from this ore, which also occurs in great abundance in the Island of Elba, and the United States of America.

Specular Iron; Red Hematite; Fer oligiste; Eisenglanz.-This mineral belongs to the fourth crystalline system, and when

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occurring in crystals, is generally found in complex modifications of the rhombohedron, among which the figures given beneath are the most common.



These crystals are of a dark steel-grey colour, opaque, except when in very thin laminæ, in which case they are translucent, and of a deep blood-red tinge.

It leaves a cherry-red or reddish-brown streak, and has a specific gravity varying from 4.8 to 5.3. Pure specular iron consists solely of peroxide of iron, of which the per-centage composition is

> Iron . . .  $\begin{array}{c} 69.34\\ \text{Oxygen} \end{array}$  Formula, Fe<sub>2</sub>O<sub>3</sub>  $\underbrace{\phantom{0}}_{100.00}$

Red iron ore presents several varieties. Fibrous iron, or red hematite, occurs in fibrous reniform masses. When the ore is amorphous, and does not present any indication of columnar structure, it is termed compact, and if contaminated with argillaceous impurities, it is known by the name of red ochre. Micaceous iron is specular iron with a foliated structure. Oligistic iron, iron glance, and rhombohedral iron, are merely other names for specular iron ore. Jaspery clay iron ore is an ore of a brownish-red colour, with a large flat conchoidal fracture. It is very compact, and has a jaspery appearance. The name of lenticular clay iron is given to this substance when it occurs in small flattened grains, resembling oolite, as at Leitmeritz and Elbogen, in Bohemia.

This ore occurs both in crystalline and stratified rocks, but the purer varieties are always found in the older formations, whilst the argillaceous ores are commonly met with in secondary rocks. Beautifully crystallised specimens are obtained from the island of Elba, where iron mines were anciently worked by the Romans; Also from St. Gothard, Arendal in Norway, in Sweden, Framont in Lorraine, Dauphiné, and Switzerland. Very brilliant crystals are also frequently formed by sublimation from the fissures of volcanic districts. Fine specimens of this kind are procured from Stromboli and Lipari, as also from Etna, Vesuvius, and Auvergne, but those from the last three districts are usually smaller than those coming from the first-named localities.

Red hematite, in reniform masses, is found in many parts of

Cornwall, at Ulverstone, in Lancashire, in Saxony, and various other localities.

Red hematite, when ground to powder, is sometimes used as a pigment, and in this state is also employed for polishing metals.

As a source of metallic iron, the peroxide is of great importance, as, from its various ores, a considerable portion of the iron manufactured in different parts of the world is obtained. It does not, however, yield so large a per-centage of metal as the magnetic oxide, and the specular varieties have the disadvantage of being somewhat refractory in the furnace. This inconvenience is obviated by a judicious mixture of other ores, when they yield iron of an excellent quality.

**Brown Iron Ore**; *Fer oxydé hydraté*; *Eisenstein.*—A mineral of a brown or brownish colour, yielding, when crushed, a yellow powder. Its density varies from 3.8 to 4.2, and when pure yields 55 per cent. of metallic iron. It usually occurs in the massive form, but varies in structure according to the locality in which it is produced.

This substance is a hydrated peroxide of iron, and is chiefly confined to the sedimentary formations. A specimen of compact brown hematite from the Lower Rhine, analysed by Vauquelin, afforded the following results :---

Peroxide o	f Iron			80.25
Water		Sector Con	1	15.00
Silica .				3.75
				in the
				99.00

This per-centage corresponds to two atoms of peroxide of iron united with three equivalents of water, and its formula will consequently be  $2Fe_3O_s+3HO$ .

This ore is frequently found in pseudomorphic forms, among which cubes and octahedrons produced by the decomposition of iron pyrites are the most common. It also not unfrequently occurs in rhombohedrons formed by the substitution of carbonate of iron, as also in moulds left by the decomposition of shells and madrepores, whose shapes the mineral consequently assumes.

It sometimes also forms stalactites, having a fibrous or compact structure, and in the centres of these, as at Oulle, pieces of metallic iron are occasionally discovered. In some localities this mineral is found in hollow reniform masses, inclosing in their centres loose globular fragments of the same substance.

*Pea iron* is one of the forms of this hydrated oxide, and is found in large deposits in the oolitic formations, where the grains are either cemented together by the same substance, or exist as detached bodies.

This mineral often occurs in an earthy state, and when naturally mixed with a considerable proportion of aluminous matter, acquires a peculiar softness of texture, and is known by the name of *yellow ochre*.

This ore is in many countries one of the most plentiful and valuable ores of iron, and is that which, in the oolitic form, supplies by far the greater number of the French iron works. In that state it is found in large quantities in Normandy, Berry, Burgundy, Lorraine, and many other places; and when washed for the purpose of separating the lighter impurities, yields an excellent material for the manufacture of iron. It is, however, remarked, that whenever the beds of oolitic iron are found to alternate with calcareous deposits, the metal produced is very brittle (cold short), and consequently unfitted for many purposes to which pure iron only can be applied. This is attributed to the presence of phosphorus, derived from the organic matter always present in chalk, and which has the property of rendering iron extremely brittle, even when present in very minute quantity.

Gothie; Fer hydroxidé; Rubin-Glimmer—is an oxide of iron containing one-half the amount of water present in the ordinary hydrated ores. This variety is comparatively rare, but occurs in the form of acicular crystals in various localities. It is found associated with quartz in the cavities of sandstone at Clifton, near Bristol; in pure black crystals at St. Just and Lostwithiel in Cornwall, also at Lake Onega in Siberia, and at Eiserfeld in Nassau.

A specimen of this substance from St. Just, analysed by Thomson, was found to be composed of—

Peroxide of i Water	ron •	•	:	•	•	:	$\begin{array}{c} 91.70 \\ 8.50 \end{array}$
						-	100.20

This corresponds to three equivalents of peroxide united to two of water, and its composition is therefore represented by the formula  $3Fe_3O_3+2HO$ .

**Iron Pyrites**; *Fer sulfuré*; *Eisenkies*, crystallises in the cubic system frequently in pentagonal dodecahedrons, also in octahedrons and cubes, more or less modified. Colour, bronze-yellow, with a metallic lustre; streak, brownish-black; specific gravity, from 4.8 to 5.1; is brittle, and strikes fire with steel; does not yield to the knife. The cleavage is parallel to the faces of the cube and octahedron: when struck, it breaks with a conchoidal uneven fracture. It consists of-

Iron .				45.74
Sulphur	 		Sec.	54.26

100.00

Or two atoms of sulphur united with one of iron, and is therefore represented by the formula FeS<sub>2</sub>.

Some of the more common forms of the crystals of this substance are represented below.



Iron pyrites occurs in small cubical crystals in veins and in various slate-rocks and coal fields, and in globular concretions imbedded in indurated clay and chalk.

It also accompanies the ores of all the other metals, and extends from the oldest primitive rocks up to the newest alluvial deposits. It usually occurs crystallised, but also in irregular masses and imitative forms; replacing, in many instances, remains of both animal and vegetable origin.

The crystals from the island of Elba are extremely large and beautiful, and often present pentagonal dodecahedrons of three or four inches in diameter. The Cornish mines furnish cubes of gigantic dimensions, and very perfect octahedrons of equal size are obtained from Sweden. Besides occurring in all districts which produce other metallic minerals, it is abundantly found in many of the coal fields, where, by its oxidation and conversion into sulphate of iron (green copperas), it sometimes produces sufficient heat to cause spontaneous ignition of the coal with which it is associated.

Iron pyrites is never metallurgically treated for the sake of the iron which it contains, but is frequently employed as a source of sulphur in manufactories of alum and sulphuric acid. When heated in the burners attached to sulphuric acid chambers, good pyrites yields about 17 per cent. of sulphur, which is burnt and oxidised in the usual way; but the sulphur thus obtained always contains arsenic. The fixed residue which remains in the retort is, after being withdrawn, thrown in heaps, and there oxidised by exposure to the air in a moist state. The sulphate of iron thus formed is from time to time removed by lixiviation, and allowed to collect in sunken receivers, from which the solution is afterwards pumped into evaporators, where the crystallisation is subsequently effected. A pigment known by the name of *colcothar*, or *purple brown*, is obtained from the undissolved matters remaining in the heaps. This mineral (iron pyrites) frequently contains small quantities of gold and silver, but these are seldom present in sufficient proportion to allow of their being profitably extracted.

White Iron Pyrites; Fer sulfure Blanc; Sparkies.—This ore has the same composition as common iron pyrites, but crystallises in forms derived from the right rhombic prism. The colour of this substance is lighter than that of the ordinary variety, and it is at the same time more liable to spontaneous decomposition. It gives a brownish-black streak, and possesses a density varying from 4.65 to 4.90. This sulphide frequently occurs in radiated crystallised masses, which, from some supposed resemblance to the comb of a cock, is called cockscomb pyrites. Large quantities of this mineral are found imbedded in the plastic clay of the brown coal formations at Littmitz and Altsattel, near Carlsbad in Bohemia, where it is employed for the manufacture of sulphuric acid and alum. It is a mineral of frequent occurrence in nearly all our mineral districts, and is often found in delicate stalactic concretions in the mines of Cornwall.

Magnetic Iron Pyrites; Pyrite magnétique; Leberkies.—This variety, which is much less common than the foregoing, is sometimes found in hexagonal prisms belonging to the fourth crystalline system, but more frequently exists in crystalline plates, as at Konigsberg in Norway, and Andreasberg in the Hartz. Crystallised specimens are, however, extremely rare, as it generally forms amorphous masses, filling the fissures of certain crystallised rocks. It has a specific gravity varying from 4.6 to 4.65, with a colour between bronze-yellow and copper-red, and leaves a dark greyish-black streak. Its composition is—

Iron .	•	•	•	•	•	59.85
Sulphur	•	·	•	•	•	40.15
						100.00

This is found to correspond to seven atoms of iron and eight of sulphur; and the mineral may therefore be regarded as a mixture of the protosulphide of iron and iron pyrites, of which the formula will be Fe S<sub>2</sub> + 6 Fe S. Although less common than the other sulphides of iron, the granular, compact, and massive varieties of this substance are far from rare, and as it is usually found associated with iron pyrites, it is sometimes employed in conjunction with that mineral for the manufacture of sulphuric acid and sulphate of iron, but is not found in sufficient quantity to be extensively applied to any useful purpose.

Arsenical Iron Pyrites; Pyrite arsenicale; Mispickel.-This mineral is frequently associated with the ores of tin, and either occurs in amorphous masses or in crystals derived from the right rhombic prism. Its colour is greyish silver white, with a metallic lustre, and granular unequal fracture. Specific gravity, from 5.7 to 6.2. Streak, greyish-black. When fused on charcoal before the blowpipe, it gives off copious white arsenical fumes, known by the characteristic smell of garlic, and the fused button that remains attracts the magnetic needle. In appearance this substance bears a certain resemblance to arsenical cobalt and greynickel, as well as to antimonial silver, but may easily be distinguished from them by the magnetic properties of the button produced on charcoal, which in the case of the other minerals enumerated does not affect the magnetic needle. Besides this, cobalt communicates a blue colour to borax; nickel gives it an apple-green tint; and from antimonial silver, a button of metallic silver is easily obtained when heated by the blowpipe on charcoal. The composition of mispickel is, according to the analysis of Chevreul-

Sulphur						20.132
Arsenic						
Iron .						34.938
						98.488

It follows from this that arsenical pyrites is an arsenio-sulphide of iron, represented by the formula Fe  $S_2 + Fe As_2$ , in which a portion of the sulphur of ordinary pyrites has been replaced by arsenic. Mispickel principally occurs in the primitive formations accompanying ores of silver, lead, and tin, and is also associated with pyrites, quartz, and blende. It is exclusively worked as an ore of arsenic, as from it the greater portion of the commercial white oxide of arsenic is prepared by sublimation. Arsenical pyrites is plentiful in some of the mining districts of Saxony, and also occurs in considerable quantities in the Hartz, Bohemia, Sweden, and at Huel Unanimity, and other Cornish mines.

Axotomous Arsenical Pyrites; Fer arsenicale Axotome.—This is a comparatively rare mineral, which, although generally found amorphous, sometimes occurs in the same forms as the foregoing. In general appearance this substance resembles mispickel; has a specific gravity varying from 7.1 to 7.4, and possesses a well defined

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cleavage parallel to the base of the prism. According to the analysis of Hoffman, this substance is composed of

Sulphur						1.94
Arsenic.						
Iron						28.06
Gangue						
0						98·16

This corresponds to two atoms of arsenic united to one equivalent of iron, and its formula will therefore be Fe As<sub>2</sub>, in which the sulphur of ordinary iron pyrites is replaced by an equivalent amount of arsenic. This ore is found associated with coppernickel at Schladming, in Styria; with serpentine at Reichenstein, in Silesia; and in a bed of sparry iron at Löling, in Carinthia.

**Carbonate of Iron**; Fer carbonaté; Eisenkalk—occurs in rhombohedrons and six-sided prisms, and may easily be mistaken for carbonate of lime, from which the crystals slightly differ in the value of their angles. Is more commonly massive, with a foliated and somewhat curved structure. Sometimes in globular concretions or lenticular masses. Colour, light-grey, but when externally decomposed becomes dark-brown or nearly black. It is usually almost opaque, with sometimes a pearly lustre, but small transparent crystals have been found in the neighbourhood of St. Austell, in Cornwall, where it occurs in scalene dodecahedrons. Streak uncoloured. Specific gravity from 3.0 to 3.85. When pure, is composed of

Protoxide of Iron					61.37
Carbonic acid	•	•			38.63
					100.00

It is consequently a carbonate of the protoxide of iron, and represented by the formula FeO, CO<sub>2</sub>. Spathose iron is found in rocks of very different ages, and is frequently observed to accompany other metallic ores, such as those of lead and copper. Carbonate of iron is, however, most plentiful in gneiss grauwacke, and the coal formations. The beds of Styria and Carinthia occur in gneiss; that of the Hartz is found in grauwacke; whilst the English deposits, from which the greater portion of the iron manufactured in this country is obtained, are exclusively confined to the coal formations. This mineral is frequently extracted from the same pits by which the coals are raised to the surface, and either occurs in reniform and lenticular septaria, imbedded in the clay found in the vicinity of the seams, or forms distinct beds alternating with those from which the coal itself is extracted. The facilities

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thus afforded to the iron manufacturer, by the presence in the same locality of the ores and the fuel required for their reduction, are evidently the chief cause of the great superiority of the iron works of Great Britain, and the low price at which that metal is produced. The principal deposits of this substance in the united kingdom are those of Dudley, the products of which are chiefly sent to Liverpool; those of Lanarkshire and Ayrshire, in Scotland; and those of Wales, which are situated on the sea coast.

All coal formations do not, however, produce iron ore; the Newcastle district, which is perhaps the richest coal field in the world, yields so little iron, that the furnaces which are worked in that neighbourhood are principally supplied by ores brought by sea from a considerable distance. The French coal fields, also, do not generally yield a sufficient amount of carbonate of iron to render its extraction a matter of importance; but to this peculiarity the basin of Aveyron is a remarkable exception, the flourishing iron works of Decazeville being supplied both with ore and coal from seams in their immediate neighbourhood. The ores treated for metallurgic purposes are always more or less impure, and usually yield from 24 to 35 per cent. of metallic iron. The following analyses, of which, those of the Scotch varieties are by Colquhoun, and the French by Berthier, show the composition of some of the more common ores accompanying the coal deposits.<sup>1</sup>

na <del>na dia 201</del> Ny taona dia Mataona dia kaominina	Cross- Basket.		Airdrie.	Bressac.	Aveyron.	St. Etienne.
Carbonic Acid.	32.53	30.76	35.17	25.5	28.9	38.4
Protoxide of			1201213	and the second		
Iron	32.22	38.80	53.03	35.0	54.2	41.8
" Manganese		0.07	to the sale	0.3	1.1	4.1
Lime	8.62	5.30	3.33	ineSlie	0.3	0.2
Magnesia .	5.19	6.70	1.77	1.6	0.9	0.3
Silica	9.56	10.87	1.40	26.5	12.8	12 3
Alumina	5.34	6.20	0.68	11.8	1.8	3.2
Peroxide of Iron	1.16	0.33	0.23	10 20 10	manne	and the second states
Carbon	2.13	1.87	3.03			
Sulphur	0.62	0.16	0.02	-	CETO BO	
Specific Gravity	3.17	3.22	3•41	3.22	3.36	3.25

Ores containing small quantities of manganese are found to produce excellent iron for the purposes of steel manufacturing, whilst the presence of a large amount of magnesia is usually detri-

<sup>1</sup> Dufrénoy, Traité de Minèralogie, vol. ii. p. 504.

mental to the quality of the metal obtained : when, however, it is merely present in small quantities, together with a portion of lime, it tends to liquify the slags, and is therefore rather advantageous.

**Chrome Iron**; Fer chromé; Eisenchrom—crystallises in the cubic system, and is sometimes found in octahedral crystals without distinct cleavage. Commonly occurs in the massive form, is of an iron-black or brownish-black colour, and when broken presents a dull uneven surface. It is slightly attracted by the magnet, has a dark-brown streak, and a density varying from 4.3 to 4.5. When fused with borax before the blowpipe this mineral communicates a fine green colour to the button. The beautiful green colour of the emerald is due to the presence of oxide of chromium.

Chrome iron appears to be essentially composed of protoxide of iron, alumina, and sesquioxide of chromium; but as the two oxides are isomorphous, they replace each other in various proportions. A specimen of crystallised chrome iron from Baltimore, U. S., analysed by Abich, afforded the following results—

Oxide of c	hro	omi	um					60.04
Protoxide	of	iro	n					20.13
Alumina								11.85
Magnesia								7.45
0								99.47

Chrome iron is ordinarily found in veins traversing serpentine rock, and occurs in Styria and the Shetland islands, where it is obtained in sufficient quantity to render it an article of export. Octahedral crystals have been meet with in New Jersey, but in its other localities it is found in the massive state only.

Amorphous chrome iron is obtained in France, Silesia, Bohemia, and Greenland. Is principally employed in the arts for the purpose of making chromate and bichromate of potash, which are used in the manufacture of various red and yellow pigments. For this purpose chrome ore in fine powder is heated in a reverberatory furnace, carbonate of potash, mixed with a portion of nitre, is occasionally added, and the mass constantly stirred to facilitate the oxidation.

By this means chromic acid is produced, which, uniting with a portion of the potash present, forms an impure chromate of potash contaminated with a certain amount of the silicate and aluminate of the same base. On removing the roasted mass from the furnace it is lixiviated with hot water, which dissolves out the whole of the soluble alkaline salts. To this solution a slight excess of nitric acid is added, which not only precipitates the silica, but by uniting with one-half its potash converts the neutral chromate into

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the bichromate, and this being much less soluble than the chromate, is easily separated by crystallisation. This salt is purified by a second crystallisation.

**Tungstate of Iron**; Schéelin ferruginé; Wolfram.—A mineral of a brown-black or iron-black colour. Occurring either in crystals derived from the rectangular or right rhombic prism, or in masses which are distinctly lamellar in one direction. It is also sometimes found in pseudomorphous forms imitative of tungstate of lime. Streak, brownish-black. Density from 6.3 to 6.8. Cleavage tolerably perfect in the direction of the laminæ. A specimen from Limoges, analysed by Ebelmen, gave the following results :—

Tungstie Acid	72.20
Protoxide of Iron	19.19
" Manganese	4.48
Magnesia	.80
	96.67

This and other analyses show this substance to be a double tungstate of iron and manganese (Fe, Mn)  $O + WO_3$ , but as the protoxides of these metals are isomorphous, they are capable of replacing each other in all proportions.

Wolfram generally accompanies tin, particularly in Cornwall, where in many places it occurs in such quantities as to materially detract from the value of the ores with which it is associated. It is also found in the tin mines of Bohemia, as well as in Greenland, Siberia, and at Limoges, in France. This mineral has been recently employed for the purpose of making tungstate of lead, which is intended to be used as a pigment instead of the ordinary carbonate at present in common use.

## ESTIMATION OF IEON, AND ITS SEPARATION FROM OTHER METALS.

For the purpose of analysis, iron is almost invariably weighed in the state of peroxide, from the weight of which the amount of metallic iron is easily deduced by calculation.<sup>1</sup> When this oxide exists ready formed in a liquid, it is best precipitated either by ammonia or its carbonate, care being taken not to operate on a cold solution, as in that case the oxide will be deposited as a hydrated gelatinous mass, extremely difficult to purify by washing. When, on the contrary, iron is present in the form of

<sup>1</sup> Peroxide of iron yields 70.0 per cent. of metallic iron.

protoxide, it is necessary before precipitation to convert it into peroxide. This may be effected either by the addition of nitric acid, and the subsequent ebullition of the solution, or by passing through it a current of chlorine gas. In the latter case the excess of chlorine is expelled by boiling, and the oxide of iron afterwards precipitated by ammonia. The oxidation of protoxide of iron may also be produced by boiling the liquor in which it is contained with hydrochloric acid and a little chlorate of potash. In this instance the oxidation is caused by the mutual decomposition of hydrochloric acid and chlorate of potash, by which chlorine being set free, produces, from its great affinity for hydrogen, the peroxidation of the iron present. When great analytical exactitude is required, it is often found advantageous to precipitate iron, either by the succinate or benzoate of ammonia, instead of employing the caustic alkali. These reagents precipitate oxide of iron much more completely than ammonia; for if this substance be added in excess, a small portion of the sesquioxide at first precipitated is redissolved in the precipitant, and the result obtained to a certain extent vitiated. The precipitated succinate or benzoate of iron is first decomposed by heating in a platinum crucible, and then weighed in the state of peroxide.

It sometimes happens that the operator is obliged to throw down the sesquioxide by the use of caustic potash added in excess. When this is done the precipitate invariably retains traces of the precipitant which can only be removed by long continued washing in distilled water. Should the quantity of iron present be large, the precipitate first obtained is most readily freed from potash, by redissolving it in dilute hydrochloric acid, carefully neutralising by ammonia and subsequent precipitation by the succinate or benzoate of that alkali. When the solution contains organic matter, such as sugar, starch, or certain of the vegetable acids, the peroxide present is no longer precipitable, either by ammonia or its carbonate, and must in that case be treated with sulphide of ammonium, which precipitates the whole of the iron in the form of sulphide. To obtain the iron in the state of sesquioxide. this precipitate should be thrown on a filter and carefully washed, care being taken to add a small quantity of sulphide of ammonium to the water, to prevent the formation of soluble sulphate of iron, which, if produced, would pass through the filter and be lost. When sufficiently washed, the matter remaining in the filter is dissolved in hydrochloric acid, the iron peroxidised by one of the methods above described, and precipitated either by succinate or benzoate of ammonia.

Iron is separated from the alkalies either by ammonia or its

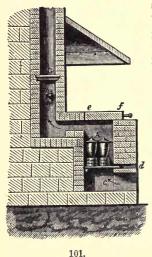
succinate. The same means are also employed for the purpose of separating that metal from the alkaline earths; but in this case it is necessary to be very particular that the ammonia employed be perfectly caustic, as should it contain any traces of carbonic acid, the precipitate necessarily becomes contaminated by the carbonates of the alkaline earths present in the solution. When oxide of iron is to be separated from magnesia, it is necessary to add such a quantity of chloride of ammonium to the liquor as will prevent the precipitation of that earth by ammonia. If, however, the solution to which ammonia is to be added contains much free hydrochloric acid, the addition of sal-ammoniac will be unnecessary, as a sufficient amount of this salt to keep the magnesia in solution will be formed on adding the ammonia.

Iron is separated from alumina by first converting it into a salt of the peroxide, and afterwards precipitating by an excess of pure caustic potash. By ebullition, the alumina, which is at first thrown down with the oxide of iron, is redissolved, and the latter will alone be precipitated. This is separated from the liquor by filtration while still hot, and the alumina subsequently obtained from the filtrate by first adding an excess of hydrochloric acid, and afterwards precipitating by carbonate of ammonia. The separation of iron from manganese is effected by the same reagents as are employed for its precipitation from solutions containing salts of magnesia. The liquor is first evaporated with nitric acid, by which the iron present is peroxidised, whilst the manganese, from the instability of the salts of its higher oxides, remains in the form of protoxide. If sufficient hydrochloric acid be not present, sal-ammoniac is now added to prevent the precipitation of oxide of manganese by ammonia, and the sesquioxide of iron is thrown down either by succinate or benzoate of ammonia, or by caustic ammonia. The precipitate is then separated by filtration, and the manganese thrown down in the state of sulphide by the addition of sulphide of ammonium. This is afterwards dissolved in a little dilute nitro-hydrochloric acid, and precipitated by carbonate of soda in the form of carbonate, which, by being strongly heated, is converted into the red oxide of manganese, in which form it is weighed. Iron may also be readily separated from manganese by another process dependent on the instability of the salts formed by the higher oxides of the latter metal. A solution containing salts of peroxide of iron is (when it contains much free acid) of a light yellow colour; but if ammonia or carbonate of soda be gradually added it slowly becomes darker, and ultimately, before any portion of the oxide is deposited, assumes a dark-brown colour. If at this point the liquor be heated to ebullition, the whole of the oxide of iron is deposited, and a clear fluid will

remain, which contains the salts of the protoxide of manganese. The oxide of iron is now to be removed by filtration, and the manganese thrown down by boiling with an excess of the precipitant originally employed. If, after the deposit of the oxide of iron, the filtrate should still remain slightly coloured, a few drops of the solution of carbonate of soda are to be cautiously added, and the liquor again boiled to separate the last traces of iron. With careful manipulation this method may be made to afford results sufficiently accurate for all commercial purposes, as the oxides having the general formula  $R_2O_3$ , are far weaker bases than those represented by RO, and consequently allow considerable latitude before the precipitation of the latter begins to take place. Where extreme accuracy is, however, required, the separation is most advantageously effected by the use of either succinate or benzoate of ammonia, added with the precautions before described.

### ASSAY OF IRON ORES.

Apparatus.—For the assay of iron ores a wind furnace, of the form shown in fig. 101, is required. This, in order that it may have a good draught, must be connected with a chimney of at least thirty feet in height, and care should be taken that no cold air be admitted into the flue by means of openings belonging to any other fire-place. Wind furnaces are usually built of such a



size that four assays may be made at the same time, by which, not only a better heat is obtained, but the loss of time and fuel attendant on the alternate heating and cooling of a large mass of brick-work is to a great extent avoided. A good size for such a furnace is 14 inches square, and 2 feet in depth from the under side of the cover, e f, to the moveable bars of iron which form the grate: these should be made of  $1\frac{1}{4}$ inch iron, and rest on two fixed bars built into the masonry of the furnace for that purpose. The ash-pit, c, is slightly raised from the floor - line for the convenience of withdrawing the incombustible cinder which falls through the bars; and the opening, d, serves for the insertion or withdrawal of the bars which constitute

the grate. The chimney, B, may be of almost any convenient size,

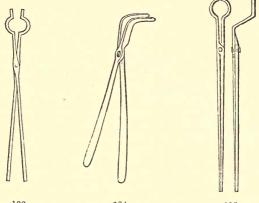
provided it is sufficiently large; but when its area is less than onehalf of that of the fire-place, A, the draught is seldom to be depended The quantity of air passing through the apparatus is reguon. lated by a damper, G, fixed in the chimney in an iron frame, and placed at a convenient distance from the ground. This is opened and shut by means of a projecting iron rod, and serves for regulating the heat of the furnace. When used, the mouth of the hearth may be closed either with an iron cover lined with firebricks, or by an ordinary fire-tile, ef. In some instances furnaces of this kind are externally lined with thick plates of cast iron, which being strongly bolted together, add greatly to the solidity of the apparatus, and at the same time prevent its being cooled by the entrance of cold air through the fissures which are liable to occur between the joints of brick-work when not thus protected. The distance allowed between the bars will depend in a great measure both on the draught and the character of the fuel which is to be employed, as when charcoal is used it is liable to crumble and fall into the ash-pit, if the space between the grate be too large. If, on the contrary, they are placed too closely together, the passage of the air is impeded, and the heat of the furnace is consequently not kept up. Coke is the fuel most commonly employed in such furnaces, and a convenient distance for the bars is in that case ‡ of an inch; but if a mixture of coke and charcoal be used, the grate should be a little closer. These arrangements are, however, easily made even after lighting the furnace, as a bar can be withdrawn with a pair of tongs through the aperture, d, and the distances of the others afterwards regulated.

The above furnace should be accompanied with an assortment of different kinds of tongs to be employed for various purposes.

For charging lumps of charcoal into hollow places, and removing hot crucibles after their withdrawal from the fire, that of the form represented, fig. 102, will be found convenient. Another kind of tongs intended for removing a crucible from the fire, either by grasping it in the bent part, or by taking one of its sides between the jaws, is represented by fig.103. Fig. 104 is of a different form, and chiefly employed for lifting uncovered crucibles, as it is only adapted for laying hold of the sides of the vessel. All these varieties are, however, straight, and rather short in the handles, and consequently merely adapted for removing bodies from the furnace when not very highly heated. For this reason, if they be employed for

102.

taking crucibles from a wind furnace of the kind just described, it will be found necessary to allow it to cool for at least an hour after the assays are completed before the crucibles can be withdrawn. To obviate this inconvenience, and prevent loss of time, the tongs represented, fig. 105, are conveniently employed. These



103.

104.

105.

being long in the handles, and provided with very strong bent jaws, may be used as soon as the crucibles are sufficiently hardened to bear removal; but as at this stage the furnace is extremely hot, it is sometimes difficult to look into the fire, in order to see



where to apply the tongs. This inconvenience is much lessened by using a wooden shield, represented by fig. 106, in which a is a small rectangular hole into which a piece of common window-glass is inserted, and b a handle by which it may be held before the face of the operator. When this shield is employed, it should be held before the person using the tongs by an assistant. By this contrivance the heat is effectually prevented from reaching the face, whilst the small glazed

aperture allows of the interior of the furnace being distinctly seen. If the opening, a, be closed by a fragment of blue or green glass, it will be found a great improvement, as the glowing crucible may then be looked at without injury to the sight.

In addition to the foregoing, it is necessary to be provided with a large cast iron mortar, a small anvil, a hammer, and a sheet of tin-plate, of which the various uses will shortly be described.

**Preliminary Operations.**—The assay of an iron ore yields on a small scale similar results to those obtained in the large way, and

consequently has the advantage over analysis, of affording information of a more practical character. Before, however, operating in the dry way, it is found necessary to obtain some definite knowledge of the mineral to be treated, in order to determine what fluxes should be added, for the purpose of affording at the same time a fusible slag, and the largest possible proportion of metallic iron. The ores of iron may be divided into three classes :--

1st. Those which chiefly consist of hydrated sesquioxide of iron.

2nd. Those which contain the metal in the state of anhydrous oxide, such as fer oligiste and magnetic iron ore.

3rd. Spathose ores, which are composed of the carbonate of the protoxide.

The preliminary examination of minerals of the first class may be conducted in the following way. A portion of the ore is selected, which as nearly as possible represents a fair average of the mineral to be treated. This is powdered in a large iron mortar, and then, in order to thoroughly mix the different particles, the whole is sifted through a sieve of coarse wire-gauze. Of this coarse powder about one thousand grains must be taken and again pounded in the iron mortar until the whole has been made to pass through a second sieve of very fine wire-gauze. The object of first pounding the whole of the sample selected, and then selecting a portion only for the purposes of the assay, is to ensure perfect uniformity of composition, and the nearest possible correspondence between the results obtained by assay and those yielded by the blast furnace in the large way. Of the finely pulverised ore, 50 grains are placed in a platinum crucible and heated to redness over a gas flame, by which means the water and carbonic acid present are driven off. The crucible and its contents are now placed in the balance, and if the weight of the calcined matter be called w, the amount of water and carbonic acid expelled will be represented by (50-w).

The calcined ore may be now thrown away, and 50 other grains taken, which are to be attacked in the cold either by acetic or very dilute nitric acid. This will dissolve only the carbonates of lime and magnesia which may be present in the gangue, without interfering with either the oxide of iron or siliceous matter. Should it not contain any earthy carbonate, no effervescence will ensue on the addition of an acid, and we may consequently pass on to the next operation; but should effervescence take place, weak acid is to be added until it entirely ceases. When this point has been attained, the residue is thrown on a filter, washed with a little water, dried and calcined. If we now call this weight w', the weight of the water, together with that of the carbonates of lime and magnesia contained in the mineral, will be represented by (50-w'), and consequently (w - w') will be the united weights of the lime and magnesia with which the carbonic acid was combined.

Lastly, 50 grains of the powdered mineral are attacked with concentrated hydrochloric acid, which is boiled until the undissolved matter which remains at the bottom of the flask has become colourless. This consists of the siliceous and argillaceous portions of the gangue, which will alone remain undissolved, and which, after being thrown on a filter and washed, are calcined and weighed. The weight of this calcined residue being represented by w'', we shall, on uniting the different results of the various operations, obtain the following information relative to the composition of the mineral:—

> Water and Carbonic Acid = (50-w)Lime and Magnesia = (w-w')Silica and Clay = w''

Oxides of Iron and Manganese = 50-(50-w)-(w-w')-w'' = (w'-w'').

If the mineral contains but a small quantity of manganese, the weight (w'-w') will represent with considerable exactitude the amount of anhydrous peroxide of iron in the ore, and will correspond to the quantity of  $\frac{56}{80}$  (w'-w') of metallic iron.<sup>1</sup>

When the ore to be examined belongs to the second class, the amount of siliceous gangue can no longer be determined by ebullition with hydrochloric acid, as the anhydrous peroxide and magnetic iron ore are very sparingly soluble in that reagent. In this case the earthy carbonates will alone be dissolved, and may be estimated by the loss sustained by boiling a known quantity of the ore in weak nitric acid, and deducting from the amount the water expelled by ignition in a platinum crucible.

Native carbonate of iron, in which the acid is combined with the protoxide, FeO, is changed by calcination into the magnetic oxide, Fe<sub>3</sub>  $O_4$ ; and, consequently, from the absorption of a portion of oxygen from the air, the loss of weight experienced during the operation will no longer represent the amount of water and carbonic acid driven off. If the mineral be treated either by acetic or dilute nitric acid, the earthy carbonates are easily dissolved; but as at the same time a portion of the iron enters into solution, the quantity of lime and magnesia which it contains cannot in this, as in the former cases, be determined by difference. It is, there-

<sup>1</sup> The presence of manganese in a hydrated ore of iron may often be detected by the colour of the mineral when pulverised. If it yield a dirty yellowish powder, it may be presumed to be tolerably free from manganese, as a very small quantity of the oxide of that metal gives it a dark-brown colour. fore, necessary to attack the pounded mineral with boiling hydrochloric acid, to which a portion of nitric acid has been added for the purpose of peroxidising the iron. The solution thus obtained is afterwards evaporated to dryness, to render the silica insoluble; and, on treating the residue with dilute acid, the soluble salts are taken up, whilst the siliceous and argillaceous matters remain undissolved, and may be separated from the liquor by filtration. From the filtrate, the oxides of iron and manganese are obtained by the use of succinate of ammonia, and sulphide of ammonium, according to the method already described.

In order to obtain the lime, the filtrate from the sulphide of manganese is first boiled, to expel the excess of sulphide of ammonium, and then treated with oxalate of ammonia, which precipitates the lime in the form of oxalate. The precipitate thus obtained, after being washed and dried, is first decomposed by calcination in a platinum crucible, and then weighed in the form of carbonate, in which state it occurs in the mineral. The amount of carbonate of magnesia present is then deduced from the weight of the pyrophosphate of that base, obtained by the addition of a solution of phosphate of soda to the filtrate from the precipitate of oxalate of lime above described. Every 100 parts of this salt is equivalent to 76.77 of carbonate of magnesia.

It has been found, by experiment, that those minerals yield the most fusible slags in which the earthy carbonates exist in the proportion of two-thirds the amount of the argillaceous and siliceous matters which they contain. The foregoing experiments, therefore, serve as a guide in the selection and quantity of the fluxes to be employed. The ores of the first and third classes require to be mixed with such quantities either of carbonate of lime or china clay as will make up the proper proportions and render the slags fusible. Those of the second class, on the contrary, seldom contain much carbonate of lime, and, as the amount of earthy matters in these ores is not very easily ascertained, it is usual to mix them with about one-third of their weight of some fusible silicate, such as light-green bottle glass. A little washed chalk is also added with advantage where no carbonate of lime occurs in the mineral, as it prevents a portion of oxide of iron from being retained by the too highly silicified slag, and the consequent loss of an equivalent amount of metal.

Method of Conducting an Assay.—The assay of iron ores is best made in crucibles lined with powdered charcoal, which not only protects the sides of the pots from being acted on by the substance treated, but also serves as the agent by which the oxides are reduced to the metallic state. On account of the high temperature to which they are subjected, it is absolutely necessary that the crucibles employed should be composed of the most refractory materials. Those usually known by the name of " London pots," and sold by the various instrument-dealers in the metropolis, are very well fitted for this purpose; but the common Cornish and Hessian crucibles will also bear the necessary heat, although of a less convenient form. In order to line a crucible, it is partially filled with coarsely powdered and slightly damped charcoal or brasque, which is then rammed into the solid form by the use of a light wooden pestle. When the first layer has become sufficiently compressed, its surface is scratched with a knife, for the purpose of making the second stratum adhere firmly to it. and a little more powdered charcoal added and beaten down as before. The surface of this layer is again rendered uneven by scratching, and the operation repeated until the crucible is completely filled. When this is the case, a cavity, of the form shown in fig. 107, is made in the centre, leaving a lining of charcoal



of about half an inch in thickness on the sides and bottom of the pot. To prevent any of the substance to be examined from adhering to the sides, the interior of the cavity is now smoothed by rubbing with a round glass pestle, and the upper edges are so rounded off as to prevent any portion of brasque from falling into the hollow during the time the mixture of ore and flux is being introduced. One hundred grains of the powdered ore are now to be well mixed on a

sheet of smooth paper, with the proper weight of flux, as indicated by the result obtained from the preliminary investigation, and then carefully transferred to the cavity in the lined crucible, where it will occupy the position b c. Any portions of the powder which may remain attached to the sides are now carefully swept to the bottom by a stiff feather, and the space, a b, filled up with powdered charcoal, and rammed as before directed. The cover, d. is now fitted, and firmly luted down with fire-clay, with which the bottom of the crucible is also cemented to pieces of fire-brick, so as to stand about four or five inches above the bars of the grate, as represented in fig. 101. When all four crucibles have been thus placed in the furnace, the damper, G, is closely shut, and a shovelful of lighted charcoal thrown between them on the grate, by which the mixture of charcoal and coke which is subsequently added becomes ignited. During the first half hour the damper remains closed, and the firing is conducted very carefully to drive off the dampness contained in the breeze, and to avoid the splitting of the luting, which would be caused were the heat too suddenly applied. At the expiration of half an hour, the damper is a little opened, and the furnace filled up with fresh coke. After

this the heat is gradually increased by still further opening the damper, and at the end of an hour it is entirely withdrawn, for the purpose of increasing the temperature to the highest possible degree. The operation, when properly conducted, should altogether require about an hour and a quarter for its completion, and at the end of that time the damper is closed, and the furnace allowed to cool. As soon as the temperature is sufficiently reduced, the crucibles are carefully removed from the hearth by the aid of proper tongs, and placed in an upright position until sufficiently cold to admit of being readily handled. They are now to be placed over a sheet of brown paper, with a view of avoiding any loss, and the lid, which will be found firmly to adhere to the pot, is removed by a blow from a small hammer. If the operation has completely succeeded, the iron will be found in a small rounded button, covered by a stratum of slag, resembling in its appearance ordinary green bottle glass, and entirely free from any adhering metallic globules. When, on the contrary, the heat has not been sufficiently great, the slag will be covered with small metallic beads firmly imbedded in its surface, from which they cannot be easily detached. If, as is sometimes the case, from want of a sufficient temperature to effect the fusion, or an improper addition of fluxes, the experiment has totally failed, the ore will be found either in a partially melted button, or merely in an agglutinated mass, in which the iron, although more or less completely reduced to the metallic state, has not formed into a distinct body. On breaking the crucible, the button, with its adhering slag, is carefully removed and crushed by a blow of the pestle in a large iron mortar. The principal button may be now readily removed; but as it seldom happens that the slag does not still enclose small metallic globules, it is necessary to reduce it to coarse powder, in order that these may be separated. This is most readily effected by turning out the contents of the mortar on a sheet of paper, and passing a magnetic bar through the pulverised slag. In this way the metallic particles are soon collected at the pole of the magnet, and, on being brushed off with a stiff feather, are placed in the balance with the larger button before separated. The iron thus obtained is not chemically pure, but invariably contains a certain proportion of carbon, which in a small degree adds to the weight, and renders the results obtained too high. This increase of weight is, however, so small as to allow of being safely neglected for all manufacturing purposes, particularly as the per-centage yield of ore in cast iron is generally that which is required to be ascertained.

In order to test the quality of iron thus obtained, the button is placed between a fold of thin tin-plate and smartly struck on an anvil by a heavy hammer. If the fracture present a mottled greyish appearance, and the button flattens slightly before breaking, the quality of the metal is considered to be good; but should it, on the contrary, split on the first blow of the hammer, and exhibit a white crystalline fracture, the ore is judged unfit for the production of the better sorts of iron.

### HUMID ASSAY.

The quantity of iron contained in any mineral soluble in acids is also readily ascertained by the use of a standard solution of the permanganate of potash. In order to do this, ten grains of the substance reduced to powder may be boiled with strong hydrochloric acid until the residual matter in the bottom of the flask has become perfectly colourless. The solution, together with the undissolved gangue, is afterwards transferred to an evaporating basin, where it is concentrated almost to dryness, for the purpose of driving off the excess of acid. Water is now added, and the siliceous matters constituting the gangue separated by filtration, and subsequently dried and weighed. To the filtrate thus obtained the standard solution of permanganate of potash is carefully added from a graduated burette, until the liquor begins to acquire a permanent rose-coloured tint, when the number of degrees which have been employed are read off, and from the amount used is calculated the quantity of iron present.

This process depends on the circumstance, that, on pouring a solution of permanganate of potash into one of a protosalt of iron, the permanganate immediately loses its colour, and is decomposed into a lower oxide, which combines with the acid, and into oxygen, which, by uniting with the protoxide of iron, converts it into peroxide. This decomposition continues as long as the liquor contains the smallest trace of a protosalt of iron; but, on the whole being peroxidised, the characteristic rose tint of the permanganate at once reappears.

In order to ascertain the strength of the standard solution employed for this purpose, six or eight grains of iron wire are dissolved by ebullition with a little hydrochloric acid, and the liquor afterwards diluted with water from which the air has been previously expelled by boiling. On adding to this from the graduated burette a sufficient amount of the solution of permanganate of potash, and noting the exact point at which the rosecolour tint makes its appearance, it is easily calculated to what amount of iron each degree of the burette corresponds, and, the strength of the liquor being thus obtained, it may afterwards be used as an assay solution. The solution of permanganate of potash is best obtained by heating a mixture of 2 parts of peroxide of manganese, 3 of caustic potash, and 1 of chlorate of potash, in an earthen crucible during two hours. The pot is then allowed to cool, and, after breaking its contents into fragments, they are treated with three or four times their weight of water, and filtered through asbestos, for the purpose of separating the sesquioxide of manganese which remains. To this filtrate weak nitric acid is cautiously added until it has assumed a fine violet tinge, when it should be immediately transferred to a well-stoppered bottle, and is, after its strength has been accurately determined, fit for immediate use.

The bottles in which this test solution is preserved must always be kept well closed, as it would otherwise soon become partially decomposed by the introduction of organic particles floating in the atmosphere.

If the ore to be examined belongs to the second class, and is, consequently, little soluble in the acids, it should be first heated in a platinum crucible, with a small quantity either of carbonate of soda or bisulphate of potash. By this treatment the mineral will be made to lose its aggregation, and is then readily attacked by the acids.

Analysis of Iron Ores.—Many of the ores of iron dissolve very readily in hydrochloric and nitro-hydrochloric acids; but in cases where the solution cannot be thus directly effected, the mineral must be first fused with an alkaline carbonate, as above directed.

To give in detail the different processes employed for the analysis of all the various ores of iron, would occupy much more space than can be here afforded them, and for this reason one of the more complicated will suffice as an illustration.

Clay iron stone is frequently found to contain at the same time all the different ingredients occurring in the various ores of iron used for manufacturing purposes, and on this account that mineral may be selected as an example. This ore ordinarily contains oxide of iron, oxide of manganese, lime, magnesia, carbonic acid, silica, and alumina, together with traces of sulphur and phosphorus. The substance should first be finely pulverised in an iron mortar, and afterwards sifted through fine wire-gauze. About thirty grains of this powder may now be intimately mixed with six times its weight of carbonate of potash or soda, or, which is better than either, a mixture of the two. This is to be kept for an hour at a full red heat in a platinum crucible, and, after being allowed to cool, is heated in a large evaporating basin containing a weak solution of hydrochloric acid. By this means the contents of the crucible will, with the exception of a small quantity

of flocculent silica, be readily dissolved with the evolution of carbonic acid gas. Should the basin not contain the amount of acid necessary to effect complete solution, more is added until no further effervescence takes place on the addition of a fresh quantity. The crucible is now withdrawn from the solution by the aid of a glass stirring-rod, care being taken to wash from it into the basin the liquor which hangs about it, as well as any portions of the flocculent silica which may remain attached. The contents of the basin are then evaporated to dryness in a sand-bath, for the purpose of rendering the silicic acid insoluble; but towards the end of the operation great care is required, in order to prevent loss by spirting, which can only be avoided by a judicious regulation of the heat and constant stirring of the pasty mass. When the evaporation is complete, the basin should be so far allowed to cool as to prevent its breaking on the addition of a cold liquid. and the residue then moistened with strong hydrochloric acid. and the whole allowed to remain for about one hour, so as to afford sufficient time for its action on the bases present. At the expiration of this period some distilled water is added, and the solution of the soluble salts aided by ebullition.

When all the soluble portions have been dissolved, the silica is separated by filtration, and, after being well washed in the filter and dried in the water-bath, is calcined and weighed as silicic The filtrate to which is added the water by which the acid. silica was washed is now neutralised with ammonia, and then treated with a slight excess of sulphide of ammonium. This reagent precipitates the iron and manganese in the form of sulphides, which are, together with the deposited alumina, to be thrown on a filter, and, to prevent the formation of soluble sulphates, washed with water containing a little sulphide of ammonium. The filtrate from these sulphides is afterwards acidified by nitric acid, boiled to expel any sulphuretted hydrogen which it may contain, and then filtered, for the purpose of separating the sulphur which has become deposited.

To the clear liquor is now added ammonia and oxalate of ammonia in slight excess, and the whole boiled until the oxalate of lime formed has collected in a dense body on the bottom of the beaker in which the precipitation has been effected. The oxalate thus obtained is afterwards collected on a filter, and then calcined and weighed as *carbonate of lime*, into which this salt is readily decomposed by heat. The *magnesia*, if any be present, is obtained from the liquor filtered from the precipitate of oxalate of lime by the addition of phosphate of soda, which throws it down in the state of ammonio-magnesian phosphate. This, after being washed, dried, and converted by ignition into pyrophosphate of magnesia, is finally weighed, every 100 parts found corresponding to 36.63 of magnesia.

To separate the *alumina*, *peroxide of iron*, and *oxide of manganese*, the mixed sulphides must be dissolved in a little hydrochloric acid to which a few drops of nitric acid have been added, and the particles of sulphur which remain unoxidised separated by filtration. The filtrate is then evaporated nearly to dryness, to expel the free acid present, and subsequently boiled with an excess of potash, by which the oxides of iron and manganese are precipitated, whilst the alumina is redissolved in the potash. The alkaline liquor is now neutralised with hydrochloric acid, and the *alumina* precipitated either by ammonia or its carbonate, and washed, dried, and weighed.

The *iron* and *manganese* may now be separated, according to the methods described, page 211; the former, being weighed as peroxide, yielding 70 per cent. of metallic iron; and the latter as red oxide of manganese, of which every 100 parts are equivalent to 72.09 of that metal. The carbonic acid present is best estimated by the method of Fresenius and Will.

A knowledge of the quantities of *sulphur* and *phosphorus* contained in an ore of iron is of the greatest importance as affecting the quality of the metal produced; and it is therefore necessary to estimate these substances with considerable accuracy.

The *sulphur* may be readily determined by either of the methods detailed, page 183, with reference to this body when present in fuels; but the most accurate results will be obtained by the first of the processes there described; for this determination, a separate quantity of the pulverised ore must necessarily be employed.

The per-centage of *phosphorus* may be determined with a greater or less degree of accuracy by various methods, but the two following will be sufficient for all the purposes of the metal-lurgist :---

Ist. If the mineral be soluble in acids, about thirty grains may be at once attacked by hydrochloric acid containing a little nitric acid; or, if it be insoluble in these reagents, it should be first fused with an alkaline carbonate. The acid solution obtained either by directly attacking the ore or by first fusing it with an alkaline carbonate, and subsequently adding acid, is evaporated to dryness, and the silica separated by filtration. The filtrate, which should not contain much free acid, is treated with ammonia in excess. The brown precipitate which forms is then to be collected on a filter, and, after being washed, is dissolved whilst still on the filter by a little dilute hydrochloric acid which has been previously heated in a flask. The liquor which passes through the filter is now poured into a stoppered bottle, and again treated with ammonia until a precipitate begins to form, when an excess of sulphide of ammonium is introduced, and the bottle, after being securely closed, is placed in a tolerably warm situation, where it is allowed to remain during twenty-four hours, at the expiration of which time the precipitated sulphides are to be separated by filtration. The phosphorus originally present in the mineral will now, in the form of phosphoric acid, be contained in the filtrate, and may be obtained and weighed as an insoluble phosphate. In order to do this, the liquor filtered from the sulphides is rendered slightly acid, and boiled to expel the hydrosulphuric acid generated. The clear liquor is now rendered alkaline by ammonia, and the phosphoric acid precipitated as ammonio-magnesian phosphate by the addition of sulphate of magnesia. Every 100 parts of calcined pyrophosphate of magnesia thus obtained represents 27.66 of phosphorus.

2d. By the second method, the amount of phosphoric acid is determined as follows1:-The compound under examination is dissolved in hydrochloric acid containing a little nitric acid, which should not be used in too great quantity, and an excess of acetate of soda is added to the solution, by which it will be made to acquire a deep red colour. On boiling, a reddish-brown precipitate is deposited, and a clear solution remains. Should the supernatant liquor still continue coloured, it is a proof either that sufficient acetate of soda is not present, or that there is an excess of iron, and a further quantity of the soda-salt is necessary. The whole is now again boiled, and, if the liquor has become clear, the brown precipitate is thrown on a filter and well washed with hot water. To obtain the phosphoric acid which it contains, the precipitate, while still moist, is dissolved in hydrochloric acid, tartaric acid is added, and subsequently ammonia, until the liquid smells distinctly of that alkali: the solution is clear, and exhibits a yellow colour. A mixture of sulphate of magnesia, sal-ammoniac, and ammonia, is now added to the solution as long as a precipitate continues to be formed. This is collected on a filter, washed with water containing a little ammonia, and, after calcination, is weighed as pyrophosphate of magnesia, as above directed. The sal-ammoniac added is for the purpose of preventing the precipitation of magnesia by ammonia, and care should be taken that the liquor from which the precipitate is obtained be distinctly alkaline.

## METALLURGY OF IRON.

Iron is employed in three different states—as *crude* or *cast iron*, as *steel*, and as *wrought iron*. The difference existing between these three substances essentially depends on the relative

<sup>1</sup> Fresenius, Quantitative Analysis, § 101.

- amounts of combined carbon with which the metal is associated. Cast iron contains a larger proportion than steel, and steel more than wrought or malleable iron, which ought to consist of pure metal without the slightest trace of carbon. In practice, this state of perfection is never obtained; but the more esteemed varieties are only found to retain extremely minute portions of carbon.

The minerals from which iron is obtained are, on account of their comparatively small value, never subjected to complicated mechanical treatment. Pea iron ore is usually agglutinated by a kind of clay containing but little iron. This is readily separated by agitating the mixture in a current of water, by which means the clay is carried off in suspension, whilst the ore, from its greater density, remains behind.

Many kinds of ore require to be roasted before they are treated for the metal they contain; by this means the water and carbonic acid present are expelled, and the ore reduced to a porous state extremely favourable to the process of smelting which it subsequently undergoes. The chief ore smelted in England is, as before stated, the argillaceous carbonate or clay ironstone of the coal measures, although a small quantity of red hematite is used as an auxiliary in some of the works in Cumberland and Lancashire; but in no instance is iron pyrites employed as a source of the metal.

The mean richness of the ores of carbonate of iron in the South Wales coal basin is estimated at 33 per cent. of cast iron, whilst those occurring in the Staffordshire district usually produce only about 30 parts of crude metal for every 100 parts of ore employed.

Every ferruginous clay-stone is an iron ore when it contains more than 20 per cent. of metal, and the average loss of water and carbonic acid by roasting generally amounts to from 25 to 30 parts in every 100 of ore calcined.

To effect the calcination of the ore, it is piled in long heaps over a stratum formed of large lumps of coal. The fire is applied at the windward end, and after it has burned a certain distance, the heap is prolonged with the same materials in the opposite direction. The ordinary height of the heap varies from about 6 to 7 feet, while its breadth at the bottom is about 15 or 20 feet. When the ore contains, as is frequently the case, a large amount of bitumen, it will, when once ignited, readily burn without any admixture of other fuel; but when it does not naturally contain a sufficient quantity of combustible matter, its place should be supplied by a sparing mixture of coal-dust. The roasting of iron ore is likewise frequently conducted in furnaces resembling ordinary lime-kilns, and in which its calcination is effected by the same means.

The proportion of fuel employed for roasting clay iron necessarily varies according to its richness in bituminous matter, but it is seldom found to calcine with less than 5 per cent., or require more than 20 per cent. of coal for this purpose.

Among the numerous coal basins existing in this country, there are two in particular which furnish more than two-thirds of the fuel annually produced in the kingdom : namely, that of Dudley in the south of Staffordshire, and that of Monmouthshire in South Wales, together with the coal-fields of Gloucestershire and Somersetshire. At Dudley, the coal, the iron ore, the limestone for flux, and the refractory clay employed in the construction of furnaces, are all associated in the same locality. The best fireclay is found at Stourbridge, and is exported thence to every part of the kingdom for the manufacture of refractory crucibles and glass-house melting-pots.

We have before seen (p. 192) that the oxide of iron is easily reduced at a red heat in an atmosphere of hydrogen gas. This reduction is equally well effected, under similar circumstances, by a current of carbonic oxide; and it is therefore evident that the reduction of the natural oxides constituting the ores of iron is attended with but little difficulty. The reduced iron is, however, in this case, intimately mixed with the refractory gangue, which prevents its particles from uniting and forming one solid mass. If the gangue were readily melted, it would be sufficient to heat the mixture to the temperature at which it enters into fusion, when the metallic sponge might be compressed by hammering, and the impurities with which it is associated squeezed out in the form of a vitreous slag. If, on the contrary, the gangue be very refractory, it can only be fused at such a temperature as causes the metallic iron produced to combine with a portion of the carbon used as fuel, and in this case the product is cast iron, instead of the malleable metal which would be otherwise obtained.

The gangue contained in the ores of iron usually consists either of quartz or clay, which are both almost completely infusible at the highest temperature of our blast furnaces. In order, then, to obtain the metal they contain, it is evident that some means must be resorted to for fluxing or rendering fusible these refractory substances. This may be effected in two different ways, varying according to the nature of the product it is desired to produce.

Should a very rich iron ore be operated on, and it be required to obtain directly a portion of malleable metal, without respect to the

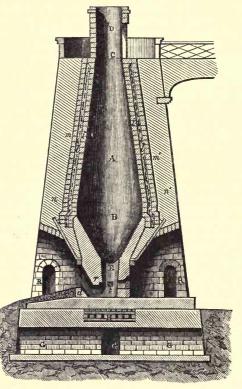
actual quantity contained in the mineral, it will be only necessary to heat the mineral in contact with charcoal or some other substances containing carbon. By this means one portion of the oxide will be reduced to the metallic state by the deoxidising influence of the fuel, whilst the other will combine with the siliceous impurities, and form an extremely fusible double silicate of alumina and protoxide of iron. It therefore follows that there is no necessity for a very elevated temperature, and, consequently, the carbon will not unite with the reduced metal, and give rise to the production of cast iron. If the fused mass be now beaten with a hammer, or compressed by being passed through a series of rollers, the fusible slag will be expressed. whilst the metallic sponge, by being subjected to strong pressure at a high temperature, becomes consolidated, and forms a compact mass. The amount of oxide of iron which by this method passes into the scoria is entirely dependent on the quantity of gangue contained in the ore, and it follows that the richer varieties only could be made directly to afford malleable iron by such treatment.

If, on the contrary, the object be the extraction of the largest possible amount of metal, without regard to the temperature employed, it will be found necessary to add to the ore some base capable of replacing the oxide of iron, which in the former instance united with silica and alumina to form a fusible slag. The only substance sufficiently cheap to admit of being employed for this purpose, is lime, which is readily obtained by the decomposition of its carbonate by heat. When lime is thus added, the resulting slag consists of a double silicate of alumina and lime, which is much less fusible than that of alumina and protoxide of iron. It therefore follows, that, to obtain the metal which the ore contains, it must be subjected to a higher temperature than would be necessary if a large portion of the oxide were allowed to remain in the slags; and consequently the iron produced combines with a certain amount of the carbon present in the furnace, and is converted into crude or cast iron.

The manufacture of iron by the former method necessitates the employment of rich ores, and from the nature of the rejected slags, the per-centage of metal obtained is far less than they are capable of yielding. The direct process nevertheless affords iron of excellent quality, and although every day becoming less extensively employed, it is still followed in the United States of America, the Pyrenees, and in some other districts, which furnish at the same time ore of great purity, and wood for the preparation of charcoal at a low price. This method of working yields a very superior metal for the manufacture of steel, and will shortly be described as the Catalan process.

## ENGLISH PROCESS OF IRON-SMELTING.

The Blast Furnace.—The great bulk of iron manufactured is at present obtained by what is called the English process; the largest possible portion of metal being extracted by treating a due admixture of iron ore and carbonate of lime, at a very elevated temperature, in an apparatus called a *blast furnace*. This is formed of



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two truncated cones, A, B, united by their bases, fig. 108. The upper portion, A, called the *cone* or *body*, is formed by an interior

#### ENGLISH PROCESS OF IRON-SMELTING.

lining of fire-bricks, i i, which is again enveloped in a casing, l l, made up of broken scoriæ, or refractory sand, and which separates the internal lining or *shirt* of the furnace from the external coating of fire-bricks, m m', supported by a mass of masonry, n n', composed either of stone or common bricks. The opening, c, at the top of the furnace, is called the *throat* or *tunnel-hole*, and is surmounted by a chimney, D, in which there are one or more openings, for the convenience of charging the fuel, ore, and flux, with which the apparatus is at regular intervals supplied. The lower cone, B, is known by the name of the *boshes*, and is either constructed of fire-brick, or of a refractory material called firestone, chiefly obtained from the coal formations.

As this part of the arrangement is subjected to a very high temperature, it is of the utmost importance that the material of which it is composed should be carefully selected, for on the durability of the boshes mainly depends the length of time during which the action of the furnace may be uninterruptedly carried on. To prevent the occurrence of a sharp angle, the two cones forming the body and boshes are united either by a curve or narrow cylindrical belt, by which the edges are slightly rounded off, and a space formed called the *belly*.

The lowest division of the furnace, E, is quadrangular in form, and composed of large slabs of refractory sandstone, cemented together with fire-clay. This is somewhat smaller at bottom than at the point E, where it meets the boshes, and its angles are gradually rounded off; but this difference of size at the two extremities is in many instances so small, as almost to give to the *hearth*, as this part is named, the form of a quadrangular prism.

The bottom of the furnace is composed of large fire-stones, supported on a mass of masonry, in which numerous channels, H, are left open for the escape of any moisture which may be expelled from the brick-work; whilst, to keep the whole building perfectly dry, the foundations are traversed by two large arched galleries, G G, which intersect each other at right angles beneath the axis of the internal cavity of the furnace.

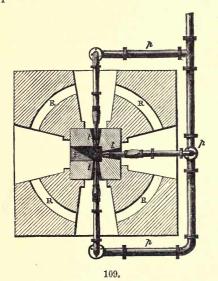
Three only of the sides of the hearth are continued to the stone constituting the bottom of the arrangement. The fourth, r, is merely brought to within a certain distance of the base, where it is supported by strong bearers of cast iron, firmly fixed into the masonry of the walls, and on which rests a heavy block of sandstone called the *tymp*.

At a distance of five or six inches beneath the tymp, and a little in advance of it, is placed the *dam-stone*, d, which has a

prismatic form, and is securely fixed by a strong piece of cast iron of peculiar shape, which covers its outer side, and is known by the name of the *dam-plate*. The part of the furnace beneath the tymp is called the *crucible*, and in it is collected the fused metal, until a sufficient quantity for tapping has been accumulated.

The face of the hearth which is opposite the dam, as well as the other two sides, are perforated a little above the level of the tymp with holes, t, into which the tuyeres are fitted, by which the blast from the blowing machine is conducted into the furnace.

In order that the workmen may be enabled to pass from one tuyere to another without loss of time, it is usual to construct four vaulted galleries, R, connecting the various arches by means of which the tuyeres and sides of the crucible are approached.



The arrangement of the tuyeres and pipes conducting the air from the blowing machine is shown in fig. 109, which represents a horizontal section of the furnace at the height of the tuyeres. Each of the pipes, p, communicating with the different tuyeres, t.t. t. is furnished either with a throttle valve or slide, worked by a screw; by the aid of which the quantity of air passing through them into the hearth is easily regulated, or, if necessary, entirely cut off. In practice it is usual to build two

or more of these blast furnaces side by side, and when the situation permits, it is found advantageous to place them at the bottom of a declivity, in such a way as to be enabled to connect their summits with the adjoining high ground by means of a bridge. By this arrangement it becomes easy to supply the furnaces with the necessary ore and fuel; but if this method, from the nature of the country, cannot be adopted, it is either raised by an inclined plane and waggons worked by the engine of the blowing machine, or by a moveable platform raised by compressed air or hydraulic pressure. The tops of the furnaces are generally enlarged by a platform, which, to prevent accidents, is railed round, and when the moveable stage is employed, the ore and other matters are raised in iron waggons, which can be readily transferred to a continuation of railway laid on the platform of the furnace, and which conducts them directly to the throat, where they are shot by tilting the waggons.

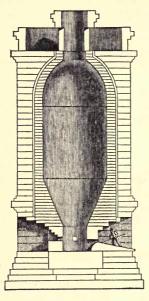
In order that the moisture may readily escape, and the brickwork be prevented from splitting, through the pressure of confined watery vapour, the whole of the masonry constituting the exterior casing of the apparatus is traversed by numerous small channels, by which the drying of the mass is greatly facilitated. The work is also strongly bound together on the outside by stout iron bands, which are made to bind tightly either by keys or screws and nuts. These horizontal bands are also held together by long vertical bars, to which they are attached by loop-eyes or strong screw-bolts, and by this means great strength and solidity are communicated to the building.

The dimensions of these furnaces differ very much according to the nature of the product which is sought to be produced, and the richness of the ores operated on. The height is extremely variable, some being only 36 feet high, including the chimney; whilst others reach an elevation of 60, and even 70 feet, from the ground.

The most common height is, however, from 45 to 50 feet, to which must be added that of the chimney, which is from 8 to 10 feet in length, and frequently formed of but one course of bricks, strongly bound together by stout iron rings and girders. In some instances these chimneys are so firmly ironed that their surface is half covered with metal; two doorways are usually left on the opposite sides of the base, for the introduction of the ore and fuel. The throat is protected and held together by a large annular plate of cast iron, and on this the foundations of the chimney repose.

The inclination of the boshes will depend on the nature of the cast iron which it is desired to produce, as its quality appears to be much influenced by the slope given to this part of the furnace.

Where very dark iron for the purposes of casting is manufactured, they are commonly less sloped than when grey iron for



110.

subsequent conversion into bars is required. The limit of this

difference is generally about 5°, the usual angle formed by the sides of the boshes with the perpendicular being from  $55^{\circ}$  to  $60^{\circ}$ .

The erection of a pair of blast furnaces of 40 feet in height requires 320,000 common bricks for the outside masonry, and 80,000 fire-bricks for the refractory lining on the inside.

In the neighbourhood of Glasgow, and in other localities where the hot blast is used, the body of the furnace is usually made of a cylindrical form, as represented in figure 110.

In South Wales, and particularly in the neighbourhood of Pentypool, the furnaces are of a much less massive construction, as the upper and lighter portions of the work are composed of a single thickness of bricks only. These are 20 inches in length, and made to suit the various curves of the furnace. The whole apparatus is strongly bound

together by a proper arrangement of iron stays, and is found to be quite as durable as those built with an external coating of heavy masonry.

The tuyeres built into the hearth of a blast-furnace are conical tubes of cast iron, a, b, c, d, fig. 111. To prevent these from being



<sup>111.</sup> 

melted by the intense heat to which they are subjected, an annular space is preserved in the metal composing the sides of the cone. Through this opening a current of cold water is constantly made to circulate, by means of two tubes, t, t', one of which, t, supplies the

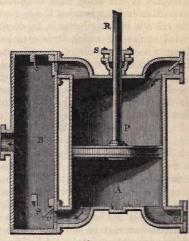
cold water, whilst the other, t', carries off that which has become heated. In these are placed the nozzles, N, made either of thin copper or sheet iron, and being connected by leathern hose, or

#### ENGLISH PROCESS OF IRON-SMELTING.

otherwise, with the pipes leading from the blowing machine, which supplies air to the furnace, they admit of being readily moved for the proper adjustment of the blast. The three tuyeres situated in the different sides of the hearth, although placed at the same height from the bottom, are not set exactly at right angles to the faces of the crucible, but are slightly inclined in opposite directions, to prevent the different currents of air from coming in contact with each other.

Blowing Machine.—The blowing machine ordinarily employed, fig. 112, consists of a large cast iron cylinder, A, accurately turned

on the inside, and provided with a piston, P, made air-tight by a metallic spring, or a packing of tressed hemp. The cylinder, A, is closed at both extremities by iron ends, and on the cover is the stuffingbox, s, through which passes the rod, B, connected with the piston. The cover of the cylinder is provided with two lateral openings, v v', one of which, v, communicates with the outer air. and is furnished with a valve opening towards the inside. The other, on the contrary, v', opens



112.

outwards, and communicates with a lateral chamber, B, also made of cast iron. The lower end of the cylinder is provided with similar valves and apertures : that marked v, which establishes a communication between the external air and the space beneath the piston, is furnished with a valve opening inwards, whilst the other, opening into the lateral chamber, is closed by a valve, v', shutting in an opposite direction.

The better to understand the action of this apparatus, let us suppose that the piston has been raised to its full height in the cylinder, and has begun to be again forced down. If the valves v v', are closed, the air contained in the upper part of the vessel will gradually become more and more rarified, and the difference of density between the air in this part of the cylinder, and that of the external atmosphere, will cause the value v' to apply itself firmly against the metallic surface before which it is hung.

The valve v, on the contrary, which opens inwards, will be lifted as soon as the difference between the density of the inclosed air, and that of the atmosphere, is sufficiently great to overcome the resistance caused by its mechanical adjustments; and in proportion as the piston descends, the space behind it will be occupied by a supply of atmospheric air arriving from without.

The motion which causes the air above the piston to dilate, will evidently at the same time compress that which is beneath, in proportion as it approaches the bottom of the cylinder, and causes the valve v, opening inwards, to close firmly against the polished metal surface to which it is attached; whilst that marked v', hung in a contrary direction, will open and allow the air to pass into the chamber B, from whence it escapes, through the aperture o, to the pipes connected with the different tuyeres of the furnace. In this way the upper portion of the cylinder draws the air from without during the descent of the piston, and forces that which is beneath it through the chamber into the pipes with which it is connected. When the piston is raised, the reverse of this takes place: the lower portion receives air from without, whilst the upper discharges that which it contains through the various pipes leading to the tuyeres. The machine is by this means made to throw into the furnace a nearly continuous flow of air, the only time at which the current is interrupted being that at which the piston has reached the full extent of its stroke, and before it has begun to move in a contrary direction.

As, however, it is of considerable importance that the regularity of the blast should not be impaired, the pipe leading from the chamber B is made to communicate with a large closed reservoir of wrought iron, where the variations referred to are lost through the elasticity of the air itself. The piston of the blowing machine is almost invariably worked by steam power, being attached by a parallel adjustment to the oscillating beam of an engine. In many cases each machine is provided with two blowing cylinders acting alternately at each stroke made by the beam, by which the motion is communicated. The power required to work an apparatus of this kind necessarily depends on its size, and also that of the furnace or series of furnaces which it supplies; but as an average about one horse power may be calculated for every 21 tons weekly produce of metal. At one of the large Welsh smelting establishments, the power of 350 horses is expended in blowing 12 furnaces and their respective fineries;

which, if we deduct one-eighth for the fineries, will leave for each a force of between 25 and 26 horses.<sup>1</sup>

These furnaces each consume on an average 3,600 cubic feet of air per minute, and yield a weekly product of 60 tons of cast iron : the force expended in blowing will therefore be equivalent to the power of one horse for every  $2\frac{1}{10}$ th tons of metal produced.

The great blowing cylinder at one of the largest of the South Wales iron works is 9 feet 4 inches in diameter, and 8 feet 4 inches in height. The piston has a range of 8 feet, and makes 13 strokes in a minute, which, after allowing 4 per cent. for loss by various leakages, gives by calculation the sum of 12,588 cubic feet of air expelled from the apparatus in one minute.

The pressure at which the blast is admitted into the hearth varies within considerable limits according to the season of the year and the nature of the fuel employed. In summer, the air being more rarified than in winter, will, in a given bulk, contain a less amount of oxygen; and a larger quantity is therefore blown into the furnace to produce a similar result.

With very light and easily combustible fuels, such as the various kinds of charcoal, but little pressure is used; but when a very dense fuel, such as coke, is employed, the air requires to be more strongly compressed. The small charcoal-fed furnaces of the Continent are frequently blown with a pressure not exceeding half a pound on the square inch; but this is more or less modified according to the nature of the charges with which it is supplied. For coke, the pressure varies from  $1\frac{1}{2}$  to  $3\frac{1}{2}$  pounds per square inch; but these numbers represent the extreme limits, and the average will probably be between  $2\frac{1}{2}$  and 3 pounds to the square inch.

**Smelting**.—Having described the blast furnace, and the different arrangements connected with its action, we will now proceed to the study of the various phenomena which influence the operation of smelting iron ores.

For this purpose let us suppose that the furnace is either quite new, or has been recently repaired, and it will be therefore necessary to commence by *lighting*. To prevent the masonry from being injured by a too sudden application of heat, this is begun by piling a quantity of loose fuel in the arch forming the breast of the furnace : on lighting this, the smoke and flame enter the body of the apparatus through the orifice left open between the tymp and the bottom of the crucible, as at this point of the operation the dam is left entirely open. The fire is to be thus kept up during several successive days, and as soon as the brick-work has become sufficiently heated, to prevent any fear of accident from an increase of temperature the fuel is thrown into the furnace through the throat, and allowed to rise as far as the middle of the boshes. When the drying is still further advanced, the whole internal cavity is gradually filled with the combustible which is to be employed in smelting the ore, and the blast gradually and cautiously applied. After a time the whole force of air is allowed to play into the furnace, and when the fuel has sufficiently sunk, a small charge of the mineral to be treated is thinly spread on its surface. Over this another layer of coke is placed, and when it has again sufficiently subsided, more ore and coke are successively added, until at the expiration of several days the charges of ore, which were at first extremely small, have been gradually increased to the normal proportion employed during the whole time the furnace is in fire.

It is essential to the proper working of the apparatus, that both the metal and gangue contained in the ore should be fused to a perfectly liquid state, in order that their separation may be readily effected by the difference of density. It nevertheless seldom happens that the minerals treated can be directly smelted without the addition of a proper flux, as the earthy impurities which they contain are found to exert a very unfavourable influence on the process of smelting. In most instances the gangue associated with the ores of iron consists either of quartz or clay, which are both infusible at the temperature of the blast furnace, and can only be melted at the expense of a certain portion of the oxide of iron contained in the mineral, and which, by passing off in the slags, considerably reduces the amount of metal obtained. If the mineral operated on be united to a siliceous gangue, infusible at the ordinary temperature of our furnaces, it can only be made to melt by the addition of a proper quantity of some one or more bases, with which it forms a fusible silicate at the temperature obtained. If, instead of adding a proper base to the ore, it be at once introduced into the furnace, the silicic acid present combines with a portion of the oxide of iron, and a fusible slag is produced, containing a large proportion of this oxide, whilst the product of metal will be proportionately reduced. In case of the mineral being associated with an argillaceous gangue, results of a very similar nature will be obtained. Silicate of alumina is of itself almost totally infusible in the blast furnace, but, on being heated with a mixture of iron ore, it combines with a portion of the oxide of that metal, and forms a double silicate of alumina and iron, which is much more readily fused. If a proper amount of carbonate of lime be thrown into the furnace, together with the ore, it will, during its descent through the body of the apparatus, be converted into caustic lime, which, by combining

with the silica and alumina present, gives rise to the production of a fusible double silicate of lime and alumina, in which the protoxide of iron is almost entirely replaced by the lime added. Should the gangue, on the contrary, be chiefly composed of quartz, it will be necessary to add both carbonate of lime and argillaceous matter: but instead of doing this directly by the use of limestone and clays rich in alumina, it is found more advantageous to effect the same object by a judicious mixture of such ores as contain the largest quantities of the substances required.

The minerals treated in many localities contain a large amount of carbonate of lime, and in this case it is impossible to obtain satisfactory results without a due admixture of silicate of alumina.

For this purpose clay ironstone is most frequently employed, although the same result is obtained by the use of a proper mixture of the rich silicate of protoxide of iron, obtained in some of the processes to be hereafter described.

The fusibility of the double silicate of lime and alumina is also influenced by the relative proportions of its various constituents. Those silicates are found to be most fusible in which the oxygen of the acid is double the amount of that contained in the united bases. The point of fusion is also materially affected by the relation existing between the respective amounts in which the two bases are combined; and those slags are invariably the most fusible which result from a mixture of one part of natural clay with about  $\frac{2}{3}$  of carbonate of lime. It has also been observed, that, all other circumstances being the same, the fusibility of a silicate is greater in proportion to the number of bases which it contains, and consequently a more liquid scoria is obtained by the addition of a magnesian limestone than if pure carbonate of lime were alone employed.<sup>1</sup>

A great proportion of the expense incurred in the metallurgic treatment of the ores of iron is occasioned by the large quantities of combustible consumed, and it is consequently of the highest importance to reduce as far as possible this expenditure of fuel. For this reason it is usual to increase the weight of the charges of ore until the metal produced suffers more from deterioration in quality than can be gained by economy of the combustible, and the working of the furnaces will therefore be most advantageously conducted when these limits are most nearly approached. The fuel employed in the blast furnace is either charcoal, coke, or coal, and the nature of the products obtained will be in a great degree

<sup>1</sup> The presence of magnesia in the limestone employed is thought to be prejudicial to the quality of the iron produced.

influenced by the nature of the combustible with which the apparatus is kept supplied. When charcoal is the fuel used, the amount of incombustible matter produced is very small, and besides being extremely fusible, it does not contain any ingredient detrimental to the quality of the iron manufactured. In furnaces, therefore, in which charcoal is consumed, the problem sought is the formation of the most fusible slags which can be produced; and great care is at the same time taken to exclude from the charge any impurities likely to exert an unfavourable influence on the properties of the metal obtained. The slag resulting from this method of treatment is a nearly pure double silicate of lime and alumina, containing but slight traces of protoxide of iron, and in which the oxygen of the acid is just double that of the united bases.

With coke, on the contrary, the amount of ash left is often considerable; and as the fuel frequently contains sulphide of iron, resulting from pyrites present in the coal from which it was made, the sulphur thus introduced into the furnace unites with the iron produced, and materially affects its quality. If in this case the mixture of ores were arranged so as to again give rise to the formation of a double silicate, having the same composition as that obtained in the charcoal furnace, a large proportion of the sulphur present would unite with the metal, thereby greatly deteriorating its quality, and totally unfitting it for the majority of manufacturing purposes.

Experience has shown, that when an excess of lime is under these circumstances present in the furnace, the sulphur no longer possesses a tendency to unite with the iron, but passes off in the slags in the form of sulphide of calcium. The slag resulting from this method of operating, instead of being a double silicate, in which the oxygen in the base is but half that contained in the acid, will form a silicate in which the oxygen of the base is equal to that of the acid, and is consequently more infusible than the slags produced by the charcoal furnace, and therefore requires a very high temperature in order to cause it to flow freely from the hearth. The metal manufactured by the use of coke is usually of inferior quality to that obtained from furnaces where charcoal is employed; but the great expense of the latter fuel causes it to be applied only where iron of the best sort is required.

**Chemical Action of the Blast.**—The chemical changes which occur during the process of smelting iron ores in the ordinary furnace, will be perhaps best understood by first examining the various reactions produced by the injected air during its ascent from the tuyeres to the throat, and afterwards tracing the gradual alterations effected in the ore and fuel during its slow descent through the different parts of the internal cavity of the apparatus. The ore and fuel are, as before stated, thrown into the furnace in regular strata, and descend in the same order until they reach the belly or upper part of the boshes. The temperature of the upper part, or cone, is not very considerable: in the neighbourhood of the boshes much more heat is evolved, whilst in the hearth is developed its maximum intensity.

The air thrown in to the hearth there meets with fuel in a highly incandescent state, and from the large excess of oxygen present, vigorous local combustion ensues. This combustion caused by the blast extends to about the middle of the boshes, but its activity is there much less than in the hearth itself, as the larger portion of the oxygen is already converted into carbonic acid before that point has been reached by the ascending current.

The gases which reach the upper part of the boshes are chiefly composed of nitrogen and carbonic acid, and as they have acquired an elevated temperature, communicate a portion of their heat to the combustible and mineral occupying the lower portion of the body or cone. Here, from the facility with which carbonic acid is at elevated temperatures converted by the presence of carbon into carbonic oxide, another change takes place. The heated carbonic acid, on arriving at the base of the cone, is decomposed by the fuel with which it comes in contact, and combining with a quantity of carbon equal to that which it already contains, becomes converted into carbonic oxide. Each atom of carbonic oxide thus produced occupies exactly the same space as the carbonic acid from which it was generated, and as every atom of the latter, by uniting with an atom of carbon, gives rise to two of the former, it follows that a great expansion of volume takes place. This dilatation must, according to the known laws of physics, cause the absorption of a corresponding amount of heat, so that the temperature will, instead of being increased, be considerably diminished, and whilst the boshes are at a white heat, the base of the cone will be merely red-hot.

The gases existing in this region now consist of a mixture of nitrogen and carbonic oxide, which must in their ascent traverse the heated ore and fuel contained in the higher part of the boshes and cone of the furnace. In doing this, the carbonic oxide readily acts at a high temperature on the oxide of iron, and reduces it to the metallic state, so that there is formed in this part of the arrangement a mixture of gangue, lime, and metallic iron. This reduction of iron causes the reproduction of a portion of carbonic acid, at the expense of the oxide of carbon, and another portion is derived from the carbonate of lime used as a flux, which is at this point converted into caustic lime by the expulsion of its carbonic acid. The gases which escape by the throat of the furnace therefore consist of nitrogen, carbonic oxide, and carbonic acid, together with hydrogen and carburetted hydrogen, arising from the dry distillation in the upper part of the cone, of the combustible employed as fuel, and which is never so thoroughly charred as not to yield a certain amount of these gases when subjected to an elevated temperature. The quantity of carbonic oxide and hydrogen is also slightly augmented by the moisture which enters with the blast through the tuyeres, and is decomposed by traversing the layers of heated fuel contained in the body of the furnace. The gases which escape from the chinney are seldom very highly heated, but are exceedingly combustible, and on being ignited burn with a clear transparent flame, which continues during the whole time the furnace is in action.

The following Tables exhibit the per-centage composition of the gases issuing from the furnaces of Vickerhagen, in Germany, and Baerum, in Norway. The ore in both these localities is treated by the aid of wood charcoal, and the gases were obtained from various distances below the throat or tunnel-hole, by passing a wrought iron pipe to the depth at which it was desired to examine the products of combustion. To the upper extremity of this tube was connected a leaden pipe, by which the gases were conducted to a place suited for their analysis, and by this means were readily collected in sealed glass tubes, from which they could be subsequently transferred into vessels properly graduated for eudiometrical examination. The experiments on the German furnace are by Professor Bunsen, and those made at the Bacrum Iron Works, by Scheerer and Langberg.

Height above the Tuvere.	Composition according to volume of the Gases at Vickerhagen.								
	$17\frac{3}{4}$ ft.	$16\frac{1}{4}$	$14\frac{3}{4}$	$13\frac{1}{4}$	$11\frac{3}{4}$	$8\frac{3}{4}$	$5\frac{3}{4}$		
Nitrogen Carbonic Acid Light Carburetted } Hydrogen . } Hydrogen, .	62·34 8·77 24·20 3·36 1·33 100·00	62·25 11·14 22·24 3·10 1·27 100·00	3.22 25.77 4.04 0.58	30.08	3.60 29.27 1.07 2.17	7.57	26 51 1.88 1.06		

#### ENGLISH PROCESS OF IRON-SMELTING.

Height above the Tuyere.	Composition according to volume of the Gases at Baerum.							
Tuyora	23 ft.	20 <sup>1</sup> / <sub>2</sub>	18	15 <u>1</u>	13	10		
Nitrogen	64.43	62.65	63.20	64.28	66.12	64.97		
Carbonic Acid	22.20	18.21	12.45	4.27	8.50	5.69		
Carbonic Oxide Light Carburetted Hy-	8.04	15.33	18.57	29.17	20.28	26.38		
drogen	3.87	1.28	1.27	1.23	1.18	0.00		
Hydrogen	1.46	2.53		1.05	3.92	2.96		
	100.00	100.00	100.00	100.00	100.00	100.00		

If we now examine the changes produced during the descent of the ore and fuel to the hearth, we shall find that very different chemical reactions are effected in the various parts of the furnace. In the neighbourhood of the throat the hygroscopic water will alone be driven off. When they have sunk to the distance of ten or twelve feet from the surface, the combined water of the hydrated oxide of iron begins to be expelled, whilst still a little farther down the carbonic acid both of the ore and flux is partially eliminated, and a portion of the oxide of iron becomes reduced to the metallic state. This reduction is completed, and the remainder of the carbonic acid expelled in the lower part of the cone and the commencement of the boshes. When the substances reach the lower part of the boshes, they there meet with a much more elevated temperature, and the lime added as a flux, together with the ash contained in the fuel, combines with the silica to form various double silicates, which are afterwards melted, and constitute a fusible slag.

In this region, also, the iron is exposed to intense heat in the presence of carbon, and a certain portion of this substance is consequently taken up by the metal which passes to the state of cast iron. A small quantity of silica is at the same time reduced in this part of the furnace; this decomposition is caused by the presence of iron and carbon: with the first of these the resulting silicium enters into combination, while the abstracted oxygen unites with carbon, and gives rise to the formation of carbonic acid gas.

The charge thus modified now arrives at the upper part of the hearth, where, from the intensity of the heat generated by the action of the blast on what remains of the fuel, both the silicates and the cast iron become completely fused, and fall in a liquid shower into the crucible beneath. As has been before observed, the atmosphere present in this portion of the apparatus is extremely oxidising; and it is therefore absolutely necessary that the hearth be so constructed as to cause the melted products to fall rapidly through the zone of oxidation. If the materials, on arriving at the termination of the boshes, were allowed to remain too long exposed to the oxidising influence there present, a considerable portion of the reduced metal would again be converted into oxide. and, uniting with the silicates of the gangue, pass off in the form of liquid slag. On reaching the crucible, the mixture of metal and fused silicates arrange themselves according to the order of their densities : the iron, from its greater specific gravity, occupies the lowest position in the hearth, while the lighter silicates float on its surface, and serve as a protection from all oxidating influ-The volume of slag thus produced is always five or six ences. times greater than that of the iron obtained, and consequently it soon rises to the level of the dam-plate, and flowing over, escapes on the top of the inclined plane to the ground on which the furnace is built. When the surface of these slags become pasty from cooling, and it therefore ceases to flow readily, the hardened scum is removed by means of pointed iron levers resting on the lateral plate of the incline, and which, for the purpose of affording a better fulcrum, is often coarsely notched like the teeth of a large saw.<sup>1</sup> During the time the slag is being gradually removed from the inclined plane, the cast iron is slowly accumulating in the bottom of the crucible, and, if not withdrawn at proper intervals, would ultimately rise to the height of the dam-plate, and escape by the same channel which affords egress to the fused silicates. When, however, the crucible has become nearly filled with metal, which, according to the construction of the furnace, happens either once or twice in the course of twenty-four hours, the iron is drawn off in order to make room for a fresh accumulation.

This removal of the liquid metal is called *tapping*, and is effected by piercing with a long bar a plug of clay, with which, during the previous operations, a hole communicating with the bottom of the crucible had been tightly closed. Before proceeding to tap, the workmen prepare moulds for the reception of the liquid metal, by excavating in the sand composing the floor of the workshop a series of parallel trenches connected by a channel which traverses all at right angles, and places them in communication with the hole at the bottom of the hearth, by which the liquid metal is withdrawn. The blast is now shut off from the tuyeres, and the plug of refractory clay rapidly removed: this allows the melted iron to flow into the channel communicating with the mould;

<sup>1</sup> Instead of removing the slags as here described, they are now more frequently moulded into large blocks by being allowed to flow into iron waggons running on a railway.—See Frontispiece.

here it assumes the form of semi-cylindrical bars or *pigs*, united by one of larger dimensions, called a *sow*, and from which they are easily separated by being broken off at the points of connection, which are for this reason purposely made thinner than the other parts of the bars. When the whole has been drawn off, the air is again admitted into the furnace, and the smelting operations as above described are repeated, until, from the quantity of metal accumulated, a second tapping becomes necessary.

The quality and consequent value of *pig iron* is not only modified by the form and size of the furnace from which it has been obtained, but also in a great measure depends on the nature of the ore from which it is reduced, as well as on the composition of the particular fuel with which the furnace is supplied. With minerals having the same composition, the iron produced by the employment of charcoal is generally of uniform quality, and well fitted both for the purposes of casting and conversion into malleable iron; but when the smelting is effected by the use of ordinary coke, the nature of the product is much more liable to variation. The products resulting from these different processes may be divided into three distinct classes.

1st. Grey cast iron, which, in flowing from the crucible, throws out blue scintillations, and on cooling exhibits a finely crystalline surface. This kind congeals very slowly, and when cast into pigs frequently presents smooth concave surfaces. When remelted, this metal forms an excellent material for castings, but is very soft and only moderately tenacious when first obtained from the furnace.

2nd. Mottled cast iron is somewhat lighter in colour than the preceding, and when broken presents a peculiar mottled appearance, from which it derives its name. Its structure is more open than that of the grey variety, but it makes excellent castings, particularly when the grey tinge predominates, and when of a lighter hue is advantageously employed for the manufacture of soft iron. It admits of being readily turned and filed, and takes a good polish.

3rd. White cast iron is hard and brittle, and presents a radiated lamellar fracture. On tapping, it flows sluggishly from the furnace, and throws out an abundance of brilliant white scintillations; it is so hard that it cannot be cut even by tempered steel; when refined, it yields wrought iron of bad quality, and is a sure indication of some derangement having taken place in the working of the furnace. It is only employed for coarse castings, and is never used in the construction of machinery.

In order to obtain cast iron of good quality, the charge of ore should never reach the maximum amount which the fuel is capable of reducing, as without an excess of carbon the furnace is liable, from the slightest accidental circumstance, to produce white iron, which is far too brittle to be employed for ordinary purposes.

It is also necessary that the various arrangements of a furnace should be ordered with distinct reference to the nature of the fuel with which it is to be supplied, as the form of the apparatus must be made to vary so as to suit the peculiar properties of the combustible employed. When the diameter of the hearth is small, the charges from above pass slowly into the crucible; and if a proper amount of combustible reaches this part of the furnace, the ore will remain a sufficient length of time in the region of most intense heat, to allow of the complete separation of the metal from the fusible slag with which it is associated. If, on the contrary, the fuel is of a very combustible nature, such as charcoal from the lighter kinds of wood, and a strong blast be at the same time employed, the greater portion is consumed before arriving at the proper distance from the tuyeres; and as in this case the oxidising zone is found to exist high up at the boshes, the reduced metal will consequently not remain a sufficient length of time in contact with carburising influences, to absorb the quantity necessary to give it the required degree of fluidity, and a large portion becomes reoxidised by traversing the currents of air furnished by the tuyeres. The product which thus arrives in the crucible consists of half-refined cast iron, difficult to fuse, and small in quantity, as the portions oxidised, by passing through the blast from the different nozzles, pass off in the resulting slags, under the form of the silicate of iron. The imperfectly carburetted iron thus produced frequently attaches itself to the internal lining of the furnace immediately above the tuyeres, and there becoming cooled by the current of air forced into the furnace, so interferes with the action of the apparatus as to make it necessary to extinguish the fire and remove the obstacle.

When, on the other hand, the hearth is very large, without possessing sufficient height, and the fuel is not readily combustible, or the blast feeble and insufficient, the temperature produced in the hearth will be extremely high, but that of the boshes becomes cooled below the point necessary for the successful working of the furnace. This deficiency of heat in the upper part of the furnace causes the minerals of which the charges are composed to arrive in the hearth in an incompletely prepared state; and as they have not then sufficient time to acquire the necessary temperature, the silicates produced remain in a pasty and partially fused state, by which the crucible is not unfrequently choked, and the action of the furnace seriously deranged. A somewhat similar inconvenience is sometimes caused by the density and impermeability of the minerals treated, for in this case the ore is but slightly affected by the gaseous oxide of carbon, through which it passes in its descent towards the hearth, and is consequently only reduced by actual contact with the carbonaceous matter with which the furnace is supplied. This difficulty may be in a great measure remedied by roasting the ores previous to being smelted, as they are thereby rendered more friable, and consequently expose a larger surface to the action of the reducing gases, than if passed to the furnace directly from the mine.

Blowing Out.-After a furnace has been in action a considerable period, its internal lining becomes extensively corroded through the action of the siliceous compounds constituting the slag. The parts most liable to be affected by being thus acted on are the hearth and boshes, which not only become much enlarged, but are also so unequally attacked on the different sides as to materially affect their form, and interfere with the functions they were destined to fulfil. When this takes place the working of the furnace is very unfavourably influenced, and it becomes necessary to modify the relative proportions of ore, flux, and fuel, with which it is supplied. In most instances it is expedient to increase the proportion of fuel employed; but when the amount required becomes considerably augmented, the furnace must be blown out, and its refractory lining thoroughly repaired. When this is to be done, the apparatus is charged with fuel only, until the whole of the metal and slag which it contained at the time of ceasing the addition of ore and flux is entirely drawn off; and after allowing it to become completely empty, it is left to cool during a considerable period.

The whole of the interior lining is now removed and carefully replaced, without in any way disturbing the outer coating of masonry, which is less subject to injury, and therefore seldom stands in need of repair. A well-constructed blast furnace should work from four to five years before requiring the reconstruction of its refractory lining. Some of the Welsh furnaces, and particularly those in the neighbourhood of Merthyr-Tydvil, have been known to work more than ten years without requiring any extensive repairs, and even at the expiration of this period the lower portions of the lining only have required entire reconstruction, as the superior portion of the cone, from being exposed to a lower temperature, is still less affected, and sometimes holds good for nearly forty years.

The quantity of coke required to produce a given weight of cast iron depends not only on the relative richness of the ores and combustible employed, but is also considerably influenced by the nature of the gangue with which the mineral is associated, and the form and dimensions of the furnace in which the process of smelting is carried on. When charcoal is the fuel used, every part of metal produced requires, on an average,  $1\frac{1}{2}$  parts of fuel for its preparation. In Staffordshire, from  $3\frac{1}{2}$  to 4 tons of coal, including that employed for roasting the ore, are required for the production of one ton of cast iron. In Wales the coal produces a larger per-centage of coke than that which is obtained in the above locality and each ton of cast iron is there calculated to require for its manufacture 3 tons of coal, equal to about 2.1 tons of coke, in which form it is supplied to the furnace.

Application of the Hot Blast .- The blast of cold air which constantly enters the furnace hearth, and supplies the oxygen necessary to the combustion of the fuel, evidently absorbs a portion of the heat thus generated, and prevents the temperature from ever rising beyond a certain limit, as although the introduction of a greater volume of air would increase the quantity of oxygen present, and thereby produce a more rapid combustion, yet at the same time the larger volume of cold air thus introduced must absorb more of the heat generated, and a kind of thermo-equilibrium is at length attained. The heat developed by the combustion is distributed in three different portions: one is communicated to the remaining fuel; another divided between the nitrogen of the injected air and the volatile products of combustion; and a third appropriated by the ore and flux present, and afterwards dissipated by diffusion so as to keep up a nearly equal temperature in every part of the zone, in which combustion proceeds with equal rapidity.

If, then, we suppose that two furnaces be in every respect similar, and each supplied with equal amounts of the same fuel, and an equal weight of air, in a given time, but that the one be blown with hot, and the other with cold air, we shall at once see that the temperature of the one can be raised much above that of the other. The quantity of fuel consumed during a given time will in each case be nearly equal, and consequently the amount of heat generated should be the same; but still the furnace supplied with hot air requires less heat than the other, in order to elevate the air with which it is supplied to the temperature of the interior of the hearth, and may therefore be heated proportionally hotter than that in which the bot blast is injected. It has been calculated, that by the use of the told blast at 572° Fah., instead of 60° Fah., a furnace may have its temperature increased about one-eighth; and if we therefore assume the temperature obtained by working with cold air to be on an average 2700° Fah., we find that this may be increased to 3060° Fah., making a difference of 360° in the effective heat of the furnace.

It therefore follows that many substances infusible in an apparatus blown with cold air, may readily be melted when heated air is employed. The fuel used, if of a slightly inflammable nature, would also burn more readily, as from the higher temperature at which it is brought into contact with the blast, its affinity for oxygen will be materially increased. By this means, then, we are not only enabled to melt bodies infusible in the ordinary furnace, but also to employ fuel of an inferior description.

Experience has shown, that if a furnace going well with the ordinary cold blast, be afterwards supplied with heated air, the amount of fuel added may be considerably reduced without affecting the proper working of the apparatus. The substitution of hot air, instead of cold, nevertheless materially affects the nature of the reactions which take place in the different parts of the apparatus. The amount of combustibles being diminished, and the quantity of air supplied from the tuyeres being in proportion to the weight of fuel used, it necessarily follows that the amount of gas passing through the furnace is much less in proportion to the mineral employed, than in a furnace working with a cold blast. If, then, the temperature of the hearth, notwithstanding the diminished quantity of fuel, be assumed to be the same as if cold air were employed, it follows that all the upper and middle parts of the apparatus must be cooler in furnaces where the hot blast is used, than in those in which cold air is injected. The fuel, also, from being more readily consumed when brought in contact with highly heated air, requires less time to unite with the oxygen of the blast, and the extent of the zone of maximum temperature will be therefore proportionally diminished. These causes are the means of producing a great difference in the nature of the chemical actions produced in the various parts of the furnace, and from this circumstance the products obtained by the hot blast are found to differ considerably from those yielded by the old process. When the hot blast is employed, the fuel used is generally uncoked coal.

In the year 1845, Bunsen and Playfair made an elaborate investigation relative to the different chemical changes affecting the production of cast iron in a furnace worked by hot blast, near Alfreton, in Derbyshire, and to them we are indebted for much additional information on this important subject. This furnace, which is 40 feet in height, and 11 feet in width at its widest part, is blown with air heated to 626° Fah. (330° C.) The blast is forced into the furnace under a pressure of 6.75 inches of mercury, the diameter of the nozzles being 2<sup>‡</sup> inches. The ore treated in this furnace is clay carbonate of iron, and is roasted previous to its introduction into the apparatus. The furnace is supplied with eighty charges, each consisting of 420 lbs. of calcined ore, 390 lbs. of coal, and 170 lbs. of limestone, in the course of twenty-four hours. The daily produce of cast iron is about 6 tons. The limestone is broken into pieces about the size of the fist before being thrown into the furnace. The coal and iron are charged in large lumps.

In order to collect the evolved gases, these chemists employed an iron tube of the kind described when speaking of the furnaces of Vickerhagen and Baerum; but on attempting to obtain by this means the gases from the zone in which the fusion of the ore was effected, the pipe was either much softened, or entirely melted, and it was consequently found impossible to obtain correct results below a certain depth from the throat of the apparatus. To remedy this difficulty, a small hole was bored through the solid masonry, from the front of the furnace to its internal cavity. This aperture was so pierced as to reach the hearth just beneath the boshes, at a distance of six feet from the bottom of the crucible, and two feet nine inches above the tuyeres. The gas drawn off from this opening was found to possess a strong smell of cyanogen, and on being ignited yielded the characteristic purple flame peculiar to that body. On being subjected to analysis, the cyanogen present was found to amount to 1.34 per cent. The other results, as obtained at the various depths below the top of the furnace, are here given in a tabular form, and will explain the various changes produced by the current of air during its passage from the tuyeres to the mouth of the furnace.

Depth under the Top.	I. 8 Feet.	II. 11.	111. 14.	IV. 17.	V. 20.	VI. 23.	VII. 24.	VIII. 34.
Nitrogen	54.77	52.57	50.95	55.49	60.46	58.28	56.75	58.05
Carbonic Acid	9.42	9.41	9.10	12.43	10.83	8.19	10.08	0.00
Carbonic Oxide	20.97	29.24	19.36	19.77	19.77	29.97	29.97	25.19
Light Carburet-								
ted Hydrogen	8.23	4.57	6.64	4.31	4.40	1.64	2.33	0.00
Hydrogen	6.49	9.33	12.42	7.62	4.83	4.92	. 5.65	3.18
Olefiant Gas .	0.85	0.95	1.57	1.38	0.00	0.00	0.00	0.00
Cyanogen	0.00	0.00	0.00	0.00	0.00	trace.	trace.	1.34
					!			

An examination of these tabulated results shows that light carburetted hydrogen must be considered as an essential constituent of the gaseous products of the apparatus, even at a depth of 24 feet from the surface, and, consequently, that the coking of the combustible is not thoroughly effected even at that distance from the top. It also further shows that the quantity of nitrogen is least considerable in the gaseous mixture drawn from a depth of fourteen feet, whilst at the same distance the amount of hydrogen and carburetted hydrogen is at its maximum, and we may there-

fore infer this to be the zone of most active distillation. On comparing the different quantities of carbonic oxide and carbonic acid, there appears to be, contrary to what was observed in the smaller charcoal furnaces, a complete absence of any mutual dependence in the proportions of each. In order to understand this, it is necessary to consider attentively the very different conditions under which the materials were exposed to the action of heat. It will be seen, by reference to the table, that the coal with which the furnace was supplied is not entirely deprived of its volatile carbonaceous products, and water formed by its distillation, even at a depth of 24 feet below the tunnel-hole. If, then, it be admitted, which is probably not the case, that the temperature in this part of the arrangement is never so far lowered by the gasification of the coal as to prevent the reduction of oxide of iron, and the consequent conversion of carbonic oxide into carbonic acid, still the ore will not only be exposed to the deoxidising influences of the gases produced in the furnace, but will also be subjected to the contrary action of the steam evolved from any portions of the coal which may have escaped coking in its downward passage. The method employed at Alfreton, of feeding the furnace with large unbroken masses of coal, has, therefore, the effect of simultaneously subjecting the ore to reducing and oxidising influences, and the relative amounts of carbonic acid, carbonic oxide, and hydrogen, will consequently be more or less influenced by local circumstances. Now, if we further consider the relative amounts of carbonic acid and carbonic oxide gases escaping from the tunnel-hole, it becomes necessary to look still deeper in the furnace for the causes which effect the reduction of the ores. If this reaction were accomplished, and the carbonic acid from the limestone totally expelled before the arrival of the charge at the commencement of the boshes, it follows that the whole of the gases from below this region should contain their oxygen and nitrogen in the same proportion as they exist in the air furnished by the blast, and could not have absorbed an excess of oxygen. On consulting, however, the following table, drawn up by Bunsen and Playfair, to show the relative proportions of oxygen and nitrogen collected from the Alfreton furnace, at various depths, it will be seen that this is not the case.

Depth from the	I.	II.	III.	IV.	v.	VI.	VII.	VIII.	IX.
Top.	5 Feet.	8.	11.	14.	17.	20.	23.	24.	34.
Nitrogen	79.2	79-2	79.2	79.2	79-2	79-2	79.2	79.2	79.2
Oxygen	24.9	23.6	24.6	19.5	25.7	23.7	28.2	27.7	27.8

This series of numbers indicates that the relative proportions of oxygen and nitrogen contained in the various regions of the furnace were very different from those observed in the German experiments; but it must be remembered that it will be extremely difficult to obtain a fair average of the gases existing in that part of the apparatus in which the dry distillation of the coal is most rapidly conducted. This source of error, however, disappears in the lower parts of the furnace, where the olefiant gas and higher hydrocarbons are no longer present, and the constant results obtained at the depth of 24 feet proves that below this point there is a continual evolution of carbonic acid, either expelled from the limestone used as a flux, or caused by the reduction of oxide of iron, or perhaps from these two sources united. Reasoning, however, from the average composition of the gases evolved from the materials employed in the furnace, it is most probable that the excess of carbonic acid is due to the former cause, and that the process of reduction takes place at the boshes only.

The great difference between the results obtained from the furnace at Alfreton, and those observed in the continental furnaces, will appear less surprising when we consider the temperature of the blast in each case, and the different nature of the fuel employed. In this country the low temperature of the upper portions of the hot-blast furnace arises from the great quantity of heat absorbed by the gases which are expelled during the coking of the fuel in the upper parts of the furnace, and, consequently, the point of reduction will in some measure depend on the size of the pieces of coal with which the apparatus is supplied. If these be large, they will evidently require to pass through a greater length of the heated cone than when broken into smaller masses, and, consequently, all other things being equal, the point of reduction will be lowest in the furnace in which the largest lumps are charged, and highest in that in which the fuel is most uniformly divided.

The most important feature of this investigation is the discovery of the presence of large quantities of cyanide of potassium in the lower region of the furnace. On introducing an iron pipe into the hole alluded to as being pierced in the front of the masonry above the tuyeres, large quantities of this substance were readily collected. To do this, the iron tubing, in order to prevent its being fused, was inserted to within a certain distance only of the internal cavity of the furnace, and to its outer end was attached a series of receivers in which the various products were cooled and collected. From the quantities thus obtained from a given volume of gas, it was calculated that at least 224 lbs. of cyanide of potassium were daily generated in the furnace. When the iron tube used in this experiment was withdrawn from the hole, it was found to be internally incrusted with melted cyanide of potassium, which became deliquescent on exposure to the air. The presence of these large quantities of potassium was at first ascribed to the limestone used as a flux; but, on carefully examining it, no traces of any of the salts of potash were discovered.

An average sample of the calcined ore was next analysed, and afforded the following results :---

Silica .				25.775
Peroxide of	Iron			60.242
Alumina				 6.583
Lime .				3.510
Magnesia			•	3.188
Potash				0.743
Manganese				traces
				100.041

The coal was also found to be another source of potash, and, on analysis, yielded the following per-centage amounts :----

Carbon		Particular of	13 11 10 20	CALCER A		74.98
Hydrogen		20.000	Leopus a	1.41.1		4.73
Oxygen		The first	1.108.0			10.01
Nitrogen			Unite design	105 0404.00		0.18
Water .	Telan		edutator.	Stated at		7.49
Silicates	Real		191 102 11			2.61
Potash			eq (Q.e.)			0.07
					1	C Dept dp_1
						100.07

From the quantity of ironstone consumed by the furnace every twenty-four hours being 33600 lbs., and that of coal 31200 lbs., it follows that it receives during that period 271.48 lbs. of potash, which, if transformed into cyanide of potassium, would yield 377.3 lbs. of that substance; but it would appear, from the examination of the gas drawn from the upper part of the hearth, that the whole of the potash present is not thus converted. From the facility with which ammonia is converted into cyanide of ammonium when passed over charcoal at a red heat, it might be supposed that the presence of cyanogen in the blast furnace is due to the decomposition of ammonia produced by the distillation of the coal. That this should be the case, will, however, appear quite impossible when we consider the temperature of the part of the furnace in which this substance is generated. The hearth, at which point the formation of cyanogen takes place, is the deepest and hottest

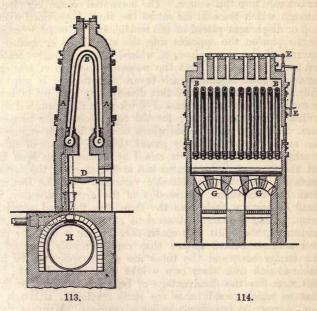
part of the furnace; and it would be therefore impossible that the coal, on arriving in that region, could still retain any traces of ammonia, as, before reaching it, it must have been exposed to a red heat for at least eight hours, during a portion of which time it is subjected to a temperature capable of reducing potassium. The same chemists have, however, shown that cyanide of potassium is produced on passing a current of nitrogen gas over a mixture of charcoal and carbonate of potash strongly heated in an iron tube, and it consequently appears certain that the cyanogen present is furnished solely by the direct union of the liberated nitrogen with a portion of the carbon constituting the fuel. Since, also, the potash will be reduced at a high temperature in the presence of carbon, it follows that the formation of cyanide of potassium in the region immediately above the tuyeres is due to the direct union of carbon with potassium and the nitrogen of the air. The presence of this substance in the hearth of the furnace cannot fail to effect extensive chemical changes, and influence to a considerable extent the reducing power of the apparatus.

It has been shown that at very elevated temperatures this salt is volatile; and if, therefore, it reaches the part of the furnace in which the reduction of the ore is effected, its high reducing properties will necessarily come into play. By this means it must become decomposed into nitrogen, carbonic acid, and carbonate of potash, of which the two former will pass off in the form of gas, whilst the latter, not being volatile, is carried down by the other materials in the furnace until it reaches the point at which it is again transformed into cyanide of potassium. In this way we can easily understand that the accumulation of cyanide of potassium may ultimately become very considerable, and capable of materially influencing the action of the apparatus. When the proportion of this salt has become increased beyond a certain amount, the excess is probably decomposed, by the action of the blast, into nitrogen and carbonic acid, which escape in the gaseous form, and into carbonate of potash, the potash of which unites with the siliceous matters present, and is carried off by the slag.

It is exceedingly difficult to determine the exact nature of the various chemical actions continually taking place in the different parts of an apparatus of such immense size, and so highly heated, as a blast furnace; but it is certain that the presence of large quantities of a material of a character so highly reducing as cyanide of potassium cannot fail to materially influence the chemical changes which are there effected. The amount of this substance is probably greater in hot-blast furnaces than in those in which air at the ordinary temperature is employed; but the quantity generated even in the cold-blast furnace must to a certain degree modify the reactions before described, and contribute to the reduction of the ores.

From the difficulties attending investigations of this description, comparatively few experiments have been made on the subject, and it is consequently impossible to assign to the different reducing agents present in the apparatus, their relative amounts of influence in the changes produced.

The apparatus by which the blast is heated to a proper temperature is usually a kind of stove, in which the air is compelled to pass through a series of cast iron pipes before arriving at the nozzles, through which it enters the furnace. Fig. 113 represents



a sectional elevation of a common form of this arrangement, and fig. 114 a vertical and lateral section of the same apparatus. A A, fig. 113, is the brick-work of the furnace; B a section of one of the syphon-shaped tubes of which the general arrangement is more clearly seen in the next figure, and of which the diameter may vary from six to eight inches; c c are horizontal pipes of considerably larger diameter than those above described, and to which the series of syphon-shaped tubes are connected by socket joints; D represents the fire-place by which the heat is supplied, and above it is a large hot air-chamber surrounding the whole of the arched pipes. The openings situated at the crown of the arched covering serve the purpose of flues for the escape of the gases coming from the fire-place, and which pass into the chamber, through a number of apertures placed in the arches, G G, fig. 114. The draught is regulated by a damper so placed as to increase or diminish the areas of these apertures, and which is readily adjusted by the compound lever, E. The large cylinder, H, is the pipe communicating with the machine by which the blast is supplied, and is of such a size as to act as a regulator, and destroy the vibrations occasioned by the oscillation of the pistons by which air is forced into the furnace. The horizontal connecting pipe,  $c_{i}$ through which the cold air enters the stove, is provided with a stop or diaphragm placed in the middle, and, in order to escape by the pipe on the opposite side, the air will be compelled to traverse the syphon pipes, B, which, being strongly heated, communicates to the blast the necessary increase of temperature. In most instances each tuyere of a furnace is provided with a heating apparatus of this description; each set of tubes is enclosed in a separate mass of brick-work, and furnished with a distinct grate and damper for the regulation of the temperature. Although in all cases where the hot blast is employed, the air is heated by being passed through a series of tubes, of which the temperature is raised by means of an open fire, yet the form of the apparatus and arrangement of the various ducts are subject to considerable variation. At the Butterly works, in Derbyshire, the section of the arched air-tubes, instead of being a circle, has the form of a flattened parallelogram, having its largest dimensions at right angles with the horizontal tubes. By this contrivance the air is made to pass over a larger heated surface than can be readily obtained in the former case, and the tubes are also supposed to be less liable to sink from their own weight when at a red heat; but this form has the disadvantage of being more expensive than that in which round tubes are alone employed, although in some respects it possesses peculiar advantages. Many of these heating stoves are made without any diaphragm in the horizontal tubes, and in this case the induction and eduction pipes are attached to opposite sides of the apparatus: they are also connected with the opposite ends of the tubes, c, and, consequently, the air first enters one of these horizontal pipes, and then, passing through the arched retorts, B, escapes to the nozzle with which it is in communication by means of a main attached to the end of the pipe placed on the other side of the fire-place. The cost of erecting the three heating stoves,

one for each tuyere of the furnace is very considerable, but they are also liable to get out of order, and each apparatus, on an average, annually requires repairs to the extent of one-fifth of its original cost.

The various arrangements of an ordinary blast furnace, including the ovens by which the heating of the blast is effected, and the waggons used for the removal of the slags, are well represented in the frontispiece of this volume, which also exhibits the method of forming the sand moulds for the reception of the liquid metal.

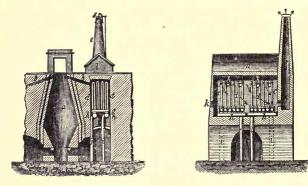
To heat the blast of a furnace producing 60 tons of cast iron per week to the required temperature (600° Fah.), the stoves will need a weekly consumption of from 30 to 35 tons of coals, or about one-half the weight of the metal produced.

## HEATING BLAST BY WASTE HEAT FROM TUNNEL-HEAD.

Since the application of the hot blast to iron furnaces, various attempts have been made to employ the waste heat escaping from the throat of the apparatus for the purpose of heating the air with which it is supplied. The importance of such an adaptation will be readily understood when we consider that in Scotland, where uncoked coal is chiefly employed, some of the largest furnaces yield from 150 to 200 tons of iron per week, and consume weekly from 300 to 400 tons of coals for its production. These furnaces receive as blast from 4,000 to 5,000 cubic feet of air per minute, and consequently vomit forth immense volumes of smoke and flame which pass uselessly into the atmosphere.

One of the methods formerly employed for the purpose of attaining this object consisted in ranging a series of iron pipes around the tunnel-head, in which the blast was heated by the flame passing out of the mouth of the furnace. In other instances the pipes were either coiled around the interior of the upper part of the cone, so as to be heated by direct contact with the ignited material which it contained, or were so enclosed in brick-work as to become heated by transmission. All these contrivances have, however, been successively abandoned, as, from the difficulty attending their repairs whenever they had got out of order, their use was found disadvantageous to the results obtained.

The great objection to all these plans for employing the waste heat arises from the circumstance that, in case of the heating apparatus becoming deranged, it becomes necessary to entirely suspend the operations of the furnace during the time it is undergoing repair; and, according to several of these plans, it would be impossible to repair a leaky joint without first blowing out the furnace with which the apparatus is connected. The best method by which, in this country, advantage is taken of the heat escaping from the tunnel-hole, is that invented by Mr. James Palmer Budd, and employed by him with great success at the Ystalyfera Iron Works in South Wales. Instead of making the heating apparatus an integral part of the furnace, the ovens are in this case so arranged as to allow of their being readily repaired without in the least interfering with the action of the furnaces with which they are connected. The stoves are built into the masonry a little below the level of the throats of the furnaces which they are intended to supply with hot air, and a chimney, 25 feet higher than the top of the platform, affords the means of drawing into them as much of the heated air and flame as may be required. These are carried from the furnace, a, fig. 115, by a series of flues, b, placed about three feet



115.

116.

below the top, and communicating with the hot air chamber, c, in which are placed the arched pipes, d, heated by the gases issuing from the furnace. The chimney, e, and its damper, f, as before stated, regulate the heat of the stove. The cross pipes, g, connect together the upright air-tubes, d, and the side pipes, h, convey the blast arriving by the upcast mains, i, to the various cross pipes. The heated air is afterwards conveyed to the tuyeres by the downcast pipes, jl. A door, k, is also placed in the brickwork of the building, l n, for the purpose of cooling the apparatus before entering it to make repairs. Fig. 116 represents a longitudinal section of the same apparatus.

With this arrangement it becomes easy to regulate the tem-

# HEATING BLAST BY WASTE HEAT FROM TUNNEL-HEAD. 257

perature to which the blast is elevated. The gases escaping from the furnace have usually a temperature of about 1800° Fah., and it is therefore necessary to draw, by the aid of the chimney, such a quantity only through the chamber as may be required to heat the air circulating in the tubes to 600°. To do this the gases should pass out of the stove at about 800°, and one-sixth part of the gaseous products issuing from the tunnel-head is found sufficient to produce the required effect. Should the temperature at any time fall too low, it may be instantly raised by slightly elevating the damper, f.

At Ystalyfera, another portion of the escaping gases is conducted through proper flues for the purpose of heating the boilers which supply the engine of the blowing machine; and even after doing this a considerable amount still goes off into the air without being applied to any useful purpose. The economy of fuel caused by the arrangement just described amounts to about one-third; so that two tons of combustible produce the same quantity of cast iron as formerly required the expenditure of three tons for its preparation. The actual quantity of fuel weekly consumed in the furnace to which this modification is applied is about 100 tons: the weight of metal obtained during the same time varies from 50 to 60 tons.

# HEAT OBTAINED BY THE COMBUSTION OF THE INFLAMMABLE GASES ISSUING FROM THE TUNNEL-HEAD.

It has been proved by experiments that the entire column of gas issuing from an iron furnace is capable of being inflamed even after it is cooled to the ordinary temperature of the air. From the results obtained by Bunsen and Playfair, during their experiments on the Alfreton furnace, they came to the conclusion that 81.54 per cent. of the heat generated is continually carried off by the unconsumed gases which escape from the chimney. From this it appears that a more than ordinary proportion of combustible matter was in this instance carried off in the gaseous state; but all chemists agree that, on an average, the quantity of heat thus lost is nearly double the amount actually developed in the cavity of the furnace itself. Several patents have at different times been taken out for methods by which the heat thus lost has been sought to be recovered and usefully applied, but the difficulties attending their employment, added to the great cheapness of fuel, has prevented their coming into use in this country, although several contrivances are still in operation in different parts of the continent, where the combustibles employed in the manufacture are less abundant, and consequently more expensive

than in Great Britain. The usual method employed for collecting these gases is by partially closing the mouth of the furnace so as to cause a slight impediment to the escape of its gaseous products, and then drawing them off by means of proper tubes to the situation where it is intended they should be consumed.

In order to do this a cylinder of cast iron of a smaller diameter than the throat of the furnace, and having a depth equal to its width, is frequently used. This is suspended by a strong flange within the tunnel-head, and as the mouth of the furnace is constantly kept charged with mineral and fuel, whilst a clear space remains between the iron collar and the lining of the furnace, it is evident that this space must be filled with the gases issuing from the apparatus, and which may be readily conducted by means of flues or iron pipes to any situation where they may be required for combustion. In furnaces built especially with a view to economising the heat to be obtained by the combustion of the unconsumed gases, the internal iron lining is often replaced by an annular flue made in the brick-work a few feet below the throat. This is connected by several arched openings with the interior of the cone, and as the charges thrown into the furnace above this point naturally offer a certain resistance to the exit of the escaping gases, they find their way into the annular flue before described, from whence they are readily drawn off in any direction in which they are required, and may be even conducted to the distance of several hundred feet.

From the quantity of nitrogen contained in these gases, it is found necessary for their combustion that they should be supplied with an artificial current of atmospheric air, and also that this should be brought in contact with the vapours to be consumed at a very elevated temperature.

In order to cool and purify the gases drawn from the cavity of the furnace, they are often passed through water; and air-pumps are frequently employed to force them towards the point where they are afterwards to be used as fuel. This gas, when once ignited, burns with the development of an intense heat, so much so as to rapidly destroy the linings of the furnace in which it is employed, unless special means be adopted to prevent the production of a too elevated local temperature. The heat thus obtained has been applied to the generation of steam for working the blowing apparatus, to the roasting of the ores, and also to refining and puddling furnaces; and although, from the cheapness of fuel in this country, the application of the combustible gases has almost ceased to be a matter of speculation, it is still probable that if a careful examination were undertaken of the various difficulties attending its employment, these might yet be overcome, and the best results obtained.

For the particulars of the various plans which are adopted on the continent to effect this purpose, I would refer the reader to the "Annales des Mines," which contains notices of all the different forms of apparatus employed.

# MOULDING CAST IRON.

The metal obtained from the blast furnace is sometimes directly conducted to the moulds, where it is to receive the form under which it is to be employed: but for the better kind of castings, and particularly when their weight is not very considerable, the metal is first run into pigs, and afterwards remelted in a furnace called a cupola, from which the fused iron is subsequently drawn off into moulds prepared for its reception.

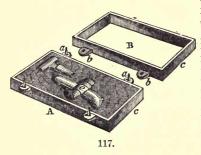
The best irons for the purposes of casting are those belonging to the first and second classes, as the white varieties are so extremely brittle as to render them unfit for the purposes of the founder. The iron best adapted for casting directly from the crucible of the furnace in which it is produced, is that known by the name of grey iron. This variety is fine in the grain, and contains but a small proportion of graphitous matter, which would, if present, tend to render the metal porous, and materially detract from its strength. The iron produced by furnaces heated by wood charcoal is, when the mineral treated is tolerably pure, invariably well calculated for casting; but where coke is employed, various precautions are necessary to be observed in order to obtain satisfactory results. In this case both the ore and fuel are liable to contain substances prejudicial to the quality of the metal, and it is therefore necessary to use a large proportion of flux, and to employ coke prepared from coal containing but little iron pyrites.

The mould into which the melted iron is poured should not only in every respect resemble in form the object to be produced, but also possess sufficient solidity to admit of the liquid metal being poured into it without changing its dimensions; and it should, moreover, be sufficiently porous to allow of the escape of the air contained in its cavities, as well as of the combustible gases generated by the action of the fused metal on the carbonaceous matter present.

The moulds employed by the iron founder are made of three different kinds of material; viz., 1, green sand; 2, baked sand; and 3, loam; but other substances are sometimes used for this purpose when the above are not considered suitable to the particular circumstances of the case.

Moulding in Green Sand.—The name of green sand is given by founders to a mixture of argillaceous sand, and pulverised coal. The former is employed in the state in which it is raised from the gravel-pit, but should be first sifted through a fine wire sieve, and afterwards intimately mixed with about one-twelfth of its volume of finely-powdered coal, and then slightly moistened with water, in order to enable it to retain the exact form of any object which may be impressed on it. When this mixture has been once employed, and consequently subjected to a high temperature, it becomes unfit for the formation of fresh moulds, and can only be used for filling up those parts of other moulds which are below the level of the cavity intended for the reception of the melted iron.

To mould an object in green sand, it is necessary to be provided with an exact model of the article to be cast. This may be made either of wood or metal, but, from not being liable to warp or shrink, the latter is generally preferred. Besides the model, or *pattern*, the founder employs a peculiarly constructed cast iron box, fig. 117, which admits of being readily separated into two



parts. In addition to its perpendicular sides, c, this box, or *flask*, as it is technically called, is, when of large dimensions, frequently provided with a series of cross bars, which support the sand and add greatly to the solidity of the mould. The two parts, A and B, of the flask may be easily separated from each other, being merely

held together by the pins, a, and the corresponding holes,  $\tilde{b}$ , which serve not only to keep the two halves always in the same relative position with regard to each other, but also afford the means of firmly joining, by the aid of suitable keys, the two portions of the iron box.

In order to obtain the form of any given model, the moulder places the part B of the flask on a platform on the level of the foundry floor, and having inverted it so that the cross bars, when there are any, may be uppermost, he fills it with sand, which he forces, by the aid of a rammer, through the spaces left between them. When this has been done, the half box is again turned, and

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as the sand with which it is filled, and which is retained in its place by friction against the sides and bars, has been strongly pressed against a smooth surface, it will necessarily itself take the same form. The workman now takes the pattern, e, from which the casting is to be made, and after having scraped a cavity roughly resembling the object to be moulded in the smooth surface of the sand, the model is as nearly as possible imbedded to one-half its thickness. The whole is now slightly sprinkled either with charcoal dust or fine sand.

This is done by shaking a bag of coarse canvas containing one of these substances in a finely divided state over the top of the flask, and the powder which is thus deposited on the surface of the model and sand in which it is imbedded, is found to prevent the adhesion of the two parts of the mould in the next operation. The part, A, of the box is afterwards lifted in its place, and is maintained in its position by the pins, a, entering into the holes, b, of the part B. The upper frame is now filled with sand, which is well and carefully rammed down, and as soon as this is accomplished, the box is turned, so that the frame, A, is placed under, and the part, B, is cautiously lifted in a vertical direction, and the two halves are again separated. The lower half, A, will now contain the pattern just half imbedded in the sand, which is generally found to fit very closely around the sides. As, however, perfect contact in all its parts is seldom thus obtained, the moulder consolidates the sand in the immediate neighbourhood of the mould by first squeezing water on it from a wet rag, and afterwards pressing it down with a small trowel. When this has been done, the support of sand prepared in the first operation is destroyed, and the flask and its contents present the appearance represented in the woodcut. At this stage of the operation, the part, B, of the box is again replaced, and after the surface of the sand contained in the lower half, A, has been again dusted to prevent adhesion, the upper part is filled with sand well rammed in as before described.

In order to make the model separate readily from the sand in which it is imbedded, it is necessary to give it a few gentle taps with some hard body, since, if this precaution were neglected, the mould, on the removal of the pattern, would present a ragged appearance from having adhered in some places to the model around which it has been pressed. To effect this, two or more strong wires are driven into the model before filling the upper part of the flask, and as these project from between the bars to a certain distance beyond the back of the box, the pattern may be readily loosened from the surrounding sand by tapping the projecting ends with a small hammer. When the enclosed model is made of metal, these wires are screwed into holes prepared for that purpose, instead of being driven, as is the case when a softer material is employed. After having thus guarded against the adhesion of the mould to the pattern, the wires are removed either by being unscrewed, or by being drawn perpendicularly out, and the moulder raises the upper half of the flask, taking the precaution to keep it in a strictly vertical position. When this has been done, it is placed on the floor of the foundry with the moulded surface upwards, and after removing with the same precautions the model from the part A, any slight imperfections in the impression are carefully repaired by the use of a little moistened sand, which is applied with iron trowels of various shapes and dimensions. If the two parts of the flask be now joined by means of the projecting pins and their corresponding holes, it will evidently contain a cavity exactly corresponding in form to the object to be produced in metal; but before the casting can be actually commenced, it is necessary to prepare proper openings for the introduction of the liquid metal and the escape of the enclosed air as well as the vapours generated during the operation. If but one aperture were employed to effect these two objects, the air could only make its escape through the same opening by which the molten metal is introduced, and the casting would consequently be subject to imperfections from portions of the former being retained in the mould. The vapours would also not have proper facilities for escape, and violent and dangerous explosions would be liable to ensue. To obviate these inconveniences, at least two orifices are made in every mould, into one of these the melted metal is poured, whilst the gases and vapours evolved from the sand find vent through the other. In order to facilitate the escape of the air, the sand itself is rendered porous by being pierced by the aid of a wire with numerous small holes, extending to within about an inch of the surface of the mould.

After preparing these gates, or openings, and carefully making good with his trowel any imperfections arising from the adhesion of sand to the pattern, the founder finely dusts with sand or charcoal by the method already described, the whole interior of the cavity, and then smooths its surface with a polished trowel.

The two parts of the mould are now joined, and, after fastening the flask together with proper keys through the pins, a, the casting may at once be proceeded with. When the pieces to be cast are very heavy, the flasks are, in the majority of cases, moved by a crane, and if the patterns are large, they are withdrawn from the sands by the joint efforts of several men, who, with one hand, lift the model by holding iron loops temporarily screwed into it, whilst with the other they tap it to prevent any portions of sand from becoming attached. When the form of a casting is complicated, it is sometimes found necessary to join together two or more flasks in order to obtain the required mould; and in cases where the thickness of metal is small, several gates are employed, as otherwise the metal would become cooled before reaching the more distant parts of the mould.

Moniding in Used or Baked Sand.—The mechanical processes employed in the preparation of moulds in baked sand are precisely similar to those used in the operation above described. When a great weight of metal is cast into moulds made of this material, it is, however, necessary to take precautions to prevent their being destroyed by the pressure to which they are subjected, as this substance being less binding in its nature than green sand, is not so well adapted for resisting the pressure occasioned by the introduction of the fused metal. To guard against this difficulty, whenever used sand is employed, the bottoms of the flasks are generally closed by iron plates firmly attached to the cross bars by means of clamps. These plates admit of being readily removed at the close of the operation, and are perforated with numerous small holes for the escape of the gases evolved.

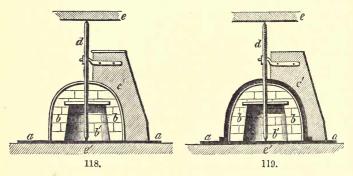
Baked sand is, in the majority of cases, used without any admixture of coal dust; and, after the completion of the mould, it is at once removed to a kind of oven, or drying-kiln, where it remains until the moisture is entirely removed, when the metal is run in whilst the sand is still hot. Castings made in this way are less liable to imperfections and air-holes than those prepared in ordinary green sand, as, from the porous nature of the material, the gases have greater facility for escaping; and as the mould is kiln-dried before the introduction of the metal, there is less chance of its becoming chilled than by the method above described. In all these manipulations the success of the several operations must, however, in a great measure depend on the skill and discrimination of the moulder, who should not only produce in the sand the exact counterpart of the object to be made, but, by a judicious mixture of his materials, so adjust his moulds that they may possess a considerable degree of tenacity, and also, at the same time, be sufficiently porous to admit of the escape of the gases which are generated on the introduction of the liquid metal.

When the object to be cast is hollow, the outer surfaces are obtained in sand as above described, and the interior cavity produced by suspending in the proper position, by wires or other contrivances, an exact model of the vacancy which is required to be produced. This model, or *core*, is generally made either of elay or loam, and, when of large dimensions, is supported by an iron centre, and rendered more tenacious by the addition of chopped hay, or some other cheap filamentary material.

**Moulding in Loam.** Moulds of this kind are made directly from drawings of the objects to be produced, as, from the nature of the material employed, the use of patterns becomes unnecessary.

The mould is formed from a mixture of clay, water, sand, and cow-hair, which, after having been reduced to the state of a hard paste, and thoroughly kneaded in a loam-mill or pug-tub, is, by the use of proper instruments, made to assume the form required. The proportions of the various ingredients are changed so as to suit the different purposes to which the loam is to be applied, and when a very light kind is required a little chopped straw, or horsedung, is usually added. This method of casting is chiefly employed for the manufacture of hollow vessels, such as boilers, sugarpans, and lead pots, in which the thickness of the metal is very inconsiderable when compared with the other dimensions of the casting. The preparation of loam moulds is, in many instances, a complicated operation, as the workman has frequently to model a considerable portion of his work without any sort of guide, except his own correctness of eye, by which to regulate his tools.

When, however, the object to be made is so formed as to admit of being produced by the revolution of a moveable arm or scraper, as shown in figs. 118 and 119, the work becomes much simplified,



as the mould may be in this way readily traced by the surfaces of revolution obtained from two different arms.

In order to produce a vessel of the form shown in fig. 120, which represents an ordinary lead melting-pot, a flat cast iron ring, a a, fig. 118, is first laid in a truly horizontal position on the floor of

the casting house. On this the workman builds a hollow brick dome, b, approaching in some measure to the form of the internal surface of the object to be moulded, and on it a thick coating of prepared loam is subsequently spread by a trowel. When this has been done, its surface is again covered



to the thickness of about an inch with another stratum of loam, which, from having been sifted through a fine sieve before mixing, is finer and closer in its texture than that employed to cover the brick-work above described. The board c, so shaped as to exactly represent the curve of the internal surface of the pan, is now attached to the vertical axis, d, which is retained in its proper position by entering a hole in the bar, e, whilst it rests at e' in a cross bar of iron passing through the diameter of the metallic ring which forms the foundation of the brick dome. This arrangement, after having been adjusted so that the rod d is truly vertical, will, on causing the arm c to revolve on its axis, produce a surface of the vessel to be obtained.

By this means the redundant clay applied to the surface of the dome is scraped off, and an exact mould of the interior of the pan readily formed. At this stage of the operation, some small coal which during the building of the brick dome, b, has been introduced into the cavity, b', is ignited by means of openings left under the cast iron ring, a a, which serve the double purpose of chimnies for the escape of the smoke, and also of air-holes by which the fire receives its draught. The combustion of the coal must, however, be conducted very slowly, as the loam would otherwise be liable to crack, and render the mould useless. The activity of the combustion is regulated by opening or closing the draught-holes left under the iron ring, which, being formed in sand, are readily so adjusted as to admit no more than the required amount of air. As the surface of the mould begins to dry, it is thickly painted over with charcoal-dust and clay, so mixed with water as to admit of being readily applied with a brush. This is done to prevent the adhesion of the second layer of loam. which is now to be applied. As soon as the surface has been sufficiently coated with the mixture above named, a second layer is applied over the whole surface of the mould, the thickness being regulated by that of the casting to be manufactured. The board, c, is now removed from the spindle, d, and another, c', fig. 119, attached to it, of which the surface corresponds to the other side of the object to be produced. By again turning the spindle,

d, with this second form attached, another surface of revolution is obtained; and, as the excess of loam will be at the same time removed, a figure is produced exactly corresponding in form to the outer side of the object to be cast. The vertical spindle, d, is now removed, and the hole through which it passed into the brick-work being left open, serves as a chimney for the smoke and gases produced by the combustion of the coal.

As soon as this new surface begins to dry, it is, like the former one, thickly painted over with a mixture of clay and powdered charcoal, in order to prevent its adherence to the third coating which is now to be applied. Another cast iron ring, similar to the one before described, but without any cross bar, is then laid down and adjusted to the former by the aid of pin-points. The surface obtained by the revolution of the last model is now covered by hand with a stratum of about two inches of fine loam, which, after being well kneaded together and smoothed over, is again covered with a dome of solid masonry, which rests on the second iron ring. After this is completed, a small hole is made through its centre for the passage of the escaping gases, and the fire is kept up until the whole mass has become completely dry, when chains are adapted to bolt-holes perforated in the second annular plate, which, together with the dome of masonry which it supports, is carefully lifted off. The convex surface, which is now laid bare, and corresponds to the outside of the casting to be formed, has, on account of the thin coating of clay and charcoal, separated readily from the dome lifted off on the second ring; and, as a similar stratum of the same substance is interposed between its other surface and that representing the inside of the pot, it follows that the thin coating corresponding to the thickness of the metal in the casting may readily be removed without injury to the two surfaces by which it is bounded. This thin coating of loam is then carefully broken away, and, after stopping the hole left by the spindle, d, and repairing any slight imperfections which may occur, the dome is again lifted in its place, and the liquid metal poured in through an opening left in the brick-work for that purpose. In this case, as well as when sand is employed, it is found necessary to leave proper apertures for the escape of the enclosed air and gases.

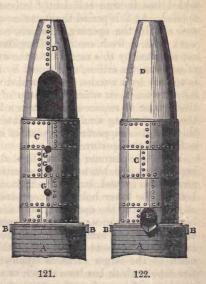
When castings with particularly hard surfaces are required, metallic moulds are sometimes employed, as from the rapidity with which these lose their heat, the iron poured into them is found exteriorly to acquire a peculiar hardness.

Second Fusion of Cast Iron.—The iron employed for casting by second fusion should contain a considerable amount of carbon, as, from the circumstance of a portion of this substance being oxidised during each operation, the metal would otherwise become very difficult to fuse, and be liable to obstruct the furnace in which the melting is effected.

For melting cast iron, a small blast furnace, called a cupola, is employed. These cupolas vary in size according to the quantities of metal they are destined to melt at one time, but the same principles of construction are in all cases invariably observed. The furnace consists of an iron casing, internally lined with brick or argillaceous sand, and is supplied with air by one or more tuyeres connected with a rapidly revolving fan.

In the older cupolas, the exterior casing was formed of cast iron slabs bound closely together by strong wrought iron bands, and in this case the furnace presented the appearance of an octagonal prism placed perpendicularly on a strong foundation of brick-work. In the newer furnaces, however, the form is usually cylindrical, as the casing is now made of thick sheets of iron, firmly united by strong rivets similar to those employed in the construction of steam-boilers. A convenient furnace of this kind is represented in the annexed woodcuts, of which fig. 121 shows a

back elevation, and fig. 122 a front view. The mass of brick-work, A, is elevated about two feet from the floor of the castingshop, and on the top of this is firmly bedded a strong cast iron plate, B, which serves for the foundation of the furnace. The cylinder, c, forming the body of the cupola, is thickly lined on the inside with fire-clay, and is surmounted by a conical hood, D, of thinner iron, which is connected with an external chimney, and carries off the smoke evolved from the apparatus when in action. The hole, E, is used for drawing off the fused



metal into moulds prepared for its reception, and is provided with a small iron gutter, E', for the purpose of guiding the stream of molten iron in a proper direction. The aperture in the hood is employed for the introduction of the coke and pig iron with which the cupola is at regular intervals supplied. The three openings, G, which are respectively six inches in diameter, are for the reception of the tuyeres by which the blast is supplied.

The lining of the furnace is often conducted as follows:—After having covered the bottom to the thickness of six or eight inches with a layer of argillaceous sand, which is slightly sloped towards the orifice of discharge, a wooden cylinder of the whole length of the cupola, and of a diameter a little less than the opening of the throat, is set upright in the axis of the metallic casing. Fine sand, containing a certain proportion of argillaceous matter, is now rammed tightly into the annular cavity which exists between the wooden cylinder and the sides of the furnace, and, when this is entirely filled, the core is removed, and the sandy lining cut away, so as to make the diameter of the furnace a little greater at bottom than at the upper part.

When the fire is lighted, wood is placed in the bottom of the furnace, and ignited by the aperture, E, which is left open for that purpose, and, when the coke which has been subsequently added has become sufficiently inflamed, the blast is gradually applied. At this period the flame escapes both by the tunnel-hole and also by the opening, E, which, being lined after each day's work with a fresh coating of argillaceous sand, becomes much consolidated by this means. At the expiration of about a quarter of an hour, the orifice, E, is closed by a plug of moist clay, which is applied by a wooden rod provided with an iron disc at one of its extremities, on which the lump of soft clay is stuck. When the furnace is required to contain a large body of melted metal, the clay stopping would not be of itself sufficiently secure, and in this case it is supported by a plate of iron firmly fixed against the outside of the aperture.

When the furnace is first lighted, the apertures, 6, are all kept open; the blast is first admitted through that which is nearest the ground, but, as the melted metal accumulates in the bottom, the lower holes are successively closed, and the blast is, at the close of the operation, only admitted through that placed highest in the series. Besides the openings shown in the back of the furnace, the same cupola has frequently two corresponding sets in the opposite sides, so that three distinct jets of air are often in the larger furnaces employed at the same time. In the cupola which has been chosen as an illustration, and which is capable of fusing about four tons of metal at one time, the total height of the body, c, is 9 feet, and its external diameter 5 feet. The coating of argillaceous sand will in this furnace be about 9 inches in thickness, which consequently leaves 3 feet 6 inches as its internal diameter. The distance of the first tuyere hole from the base of the cylinder is 2 feet 6 inches, whilst the others are placed at a distance of 15 inches apart. The great height of the first orifice is partly for the purpose of allowing for the lining of the bottom, and partially in order to admit of a considerable accumulation of fused metal taking place previous to raising the nozzle of the blast-pipe. The lining of a furnace lasts from five to six weeks, during which time about thirty meltings are made.

When the argillaceous coating has become much acted on, the furnace is allowed to cool, and is afterwards re-lined by the method above described. The diameter of the nozzles varies from 3 to 5 inches, and the vanes of the fan which supplies the air make from 650 to 900 revolutions per minute. When the apparatus is first lighted, no metal is thrown into it until a considerable accumulation of ignited coke has taken place in the bottom. Coke and pig iron are then ultimately charged in the proportion of about 25 of the former for every 100 parts of the latter. The iron must, before its introduction into the furnace, be broken into pieces varying from 14 lbs. to 28 lbs. in weight, and the first charge generally begins to melt in about twenty minutes after it has been thrown in. The successive charges are subsequently made at intervals of from ten to fifteen minutes, but this is more or less influenced by the dimensions of the apparatus and the quality of the metal which is being fused. When the fusion is complete, the clay plug is pierced with a pointed iron bar. The molten metal is transferred from the cupola to the moulds by two different methods. For large and heavy castings, the moulds are often sunk in the floor of the workshop, and commonly placed near the cupola, and it is therefore usual to conduct the liquid iron directly from the furnace by means of channels formed in sand. When, on the contrary, the castings are small, and the moulds situated at a considerable distance from the melted iron. it is drawn into large ladles of the form represented by fig. 123. which are lined with a siliceous

lute, and carried by the founders to the place where they have prepared the moulds to be filled with metal. During the intervals which occur between the successive castings, the tap-hole is closed by a plug of damp clay. When a heavy casting is to be made at a considerable distance from the melting furnace, larger ladles of the kind above described are employed, and these are lifted and carried to the place of their destination by means of cranes or other machinery adapted for that purpose. Every casting requires considerably more melted metal than is necessary to fill the mould. This excess goes to form the gates, false seams, &c. which are removed after the cooling of the iron, and before the castings are sent out of the foundry. Besides this there is always an actual waste of about 6 per cent. of the whole metal employed; so that, after deducting all these several items, each cwt. of coke thrown into the furnace is found to melt about 3 cwts. of ordinary pig iron.

The nozzles of the tuyeres are made so as to admit of being easily raised or lowered, to blow into the various holes in the sides of the furnace, and for this purpose they are connected with the air-pipe either by leathern hose, or, what is a much better arrangement, by telescope joints. The main is also provided with a sliding damper or throttle-valve which is placed in some convenient position in the neighbourhood of the tuyeres, and by this the founder is enabled to intercept the blast at any given moment without stopping the ventilator by which it is produced. To drive a revolving fan of the dimensions proper for furnishing the necessary supply of air for such a furnace as that which has been described, a power about equal to the force of three horses will be required.

#### MANUFACTURE OF WROUGHT IRON.

In order to transform cast iron into wrought, it is necessary to separate from it the carbon and silicium with which it is combined. To effect this object, the metal is exposed for a considerable period to the action of oxidising influences, by which the carbon is converted into carbonic acid, which escapes in the gaseous form, whilst the resulting silica unites with oxide of iron, giving rise to the formation of vitreous slags. Cast iron also frequently contains small portions of sulphur and phosphorus, which require to be carefully removed during the process of refining, as their presence in the wrought iron produced would materially affect its properties, and, if occurring in large quantities, render it entirely useless. The separation of these substances from cast iron is, however, attended with very great difficulty, and it is therefore advisable to avoid as far as possible their occurrence in the rough When the presence of sulphur is due to the nature of metal. the mineral treated, it is readily removed by a careful roasting previous to the introduction of the ore into the furnace. But if, on the contrary, the sulphur be derived from the fuel, as is frequently the case when coke made from coal containing iron pyrites is employed, it becomes necessary to charge into the furnace large quantities of carbonate of lime, which determine the

elimination of this impurity in the slags in the form of sulphide of calcium. Similar means are also employed for the removal of phosphorus, the presence of which is even more prejudicial to the manufactured iron than an equivalent amount of sulphur. When ores contain any considerable quantity of either of these substances, it is found impossible to obtain from them iron of good quality.

When a furnace only supplies iron destined for conversion into malleable metal, it is usually worked in such a way as to yield cast iron of the white variety, which, from the small amount of carbon it contains, is peculiarly adapted for the purpose. To obtain this result, the weight of mineral charged should be large in proportion to the quantity of fuel used, and the blast requires to be forced into the hearth at a high pressure, so as to determine the rapid descent of the ore. It is, however, necessary that the minerals thus treated be of good quality, and tolerably free from impurities, as otherwise an inferior kind of cast iron, quite unfit to be manufactured into bars, will be obtained.

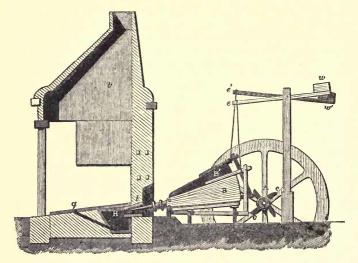
When cast iron is strongly heated in contact with air, its surface soon becomes covered with a layer of oxide. By degrees this oxide again reacts on the interior portions of the mass : the carbon which it contains reduces the oxide first formed, metallic iron is produced, and carbonic oxide gas is evolved. A similar reduction is also effected by the silicium present, which is thus converted into silicic acid, and, by combining with a portion of unreduced oxide, gives rise to the formation of a fusible silicate of iron. The composition of this silicate varies according to the relative amounts of oxide of iron and silicic acid present, but usually assumes the formula 3 FeO, SiO<sub>3</sub>, which appears to be the most stable of the compounds produced. If, in fact, a more basic silicate than this, such as 6 FeO, SiO<sub>3</sub>, for instance, be heated in contact with cast iron, a portion of the oxide becomes reduced at the expense of the carbon contained in the crude metal, and the slag is in a short time reduced to the formula given above. At very high temperatures a portion of the oxide of iron present even in slags having this composition becomes reduced; but, as in practice the heat employed is seldom sufficient to produce this effect, the usual composition may be assumed to closely correspond to that above stated.

On these reactions, then, is founded the conversion of cast iron into wrought. The iron first becomes oxidised: one portion of this oxide is again reduced by the carbon, and another combines with the silicic acid formed. These successive reactions go on until the whole mass is converted into malleable iron and fusible slag. The spongy metal is afterwards consolidated, and the silicates expressed by means shortly to be described. The silica of the slag is not, however, entirely derived from the silicium contained in the original pigs of iron, as a large portion is due to the sand which adheres to their surfaces, and is derived from the moulds in which they were cast. A source of this substance may also be traced to the ashes of the combustible by the aid of which the refining is effected, and which frequently contain a large percentage of siliceous matter.

Two different methods of conducting the refining of cast iron are extensively employed: the first, or German method, is chiefly confined to the Hartz, and is carried on by the aid of charcoal only; whilst for the second, or English process, pit coal is exclusively employed.

## REFINING BY THE GERMAN FORGE.

This operation is carried on in a small furnace, of which fig. 124 represents a vertical section, and fig. 125 the ground plan. The quadrangular hearth,  $\mathbf{H}$ , is formed of thick cast iron plates, which, for protection against the corrosive action of the slags, are subsequently coated with a lining of fire-clay. The depth of this crucible is about 10 inches, and its width from 2 feet to 2 feet 4 inches.

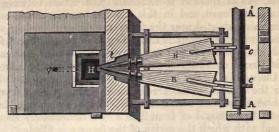


124.

The blast is conveyed into the hearth by the tuyere, t, which projects about 4 inches into it, and is so inclined that its axis may

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intersect the opposite face of the crucible, on the line of its junction with the plate forming the bottom of the arrangement.



125.

The tuyeres are composed either of sheet copper or baked clay, and are of the form represented in fig. 126. In these are placed the nozzles of the wooden bellows, B B', set in motion by a waterwheel, and so arranged as to afford a continual stream of air.

The moveable lids of these are raised by cams, c, placed on the axle, A A', of the water-wheel, and the too rapid fall of the vibrating segments is checked by their being attached to the levers, e, e', provided with boxes, w w', into which are placed weights for the purpose of regulating the rapidity of the descent. The cams, c, are so disposed around the axle of the wheel, that the moveable half of one bellows begins to be raised at the same moment as that of the other is being released, and in this way a continuous current of air is kept up in the furnace.

In front of the fire-place is a cast iron plate, raised on one side to the level of the crucible mouth, and on the other inclined to that of the refinery floor. An aperture, called the *chio* or *floss-hole*, passes through the side of the furnace, and enters the hearth at the bottom of the crucible : by this aperture the fusible slags are occasionally run off. Over the furnace is placed a hood, v, which is made of brick-work, and being provided with a chimney, serves to carry off the smoke and gases evolved during the process of refining. To the sides of this hood are attached plates of sheet iron, for the purpose of screening the workmen from the intense heat to which they would otherwise be exposed.

In order to understand the working of this furnace, let us suppose that an operation has just been terminated, and that the hearth still contains a considerable quantity of incandescent charcoal.

The workman begins by filling up the crucible with fresh fuel, and then gradually admits the blast. In the older forges the supply of air is regulated by limiting the supply of water on the wheel by which the bellows are set in motion, but in those of more recent construction blowing cylinders are employed, and in this case the blast is turned on by a proper valve situated near the tuyeres.

The iron to be refined is cast either into pigs of 6 or 8 feet in length, or into small bars or thin plates. In the first case the bar is placed on two iron rollers, and its extremity introduced into the middle of the hearth at a height of from 6 to 9 inches above the bottom of the crucible. When, on the contrary, the metal to be refined has been cast into smaller masses, they are piled to the amount of from 2 to 3 cwt. immediately above the charcoal with which the cavity of the furnace is filled.

After a short time the metal begins to melt, and passing through the current of air issuing from the tuyeres, falls to the bottom of the hearth. This period of fusion ordinarily lasts from three to four hours, and during that time advantage is taken of the intense heat developed to weld together, and form into bars, the metal refined during the preceding operation. The drops of melted iron, in passing at a high temperature through the air furnished by the tuyeres, become partially oxidised, and by a subsequent reaction of the basic silicate of iron formed, a considerable portion of their carbon is consumed.

On arriving at the bottom of the hearth, the iron thus treated has become to a certain extent decarburetted, and forms a pasty mass beneath the layer of fuel through which it has passed. The slag which gradually accumulates in the furnace is from time to time run off through the tapping hole before referred to, care being taken to retain a sufficient quantity to carry on the process of decarburisation.

The oxidation of the iron is also partially promoted by bringing the melting mass immediately before the current of air thrown in by the tuyeres. The slag run off is preserved for use in the succeeding operation.

When the partially refined *loupe* or *bloom* has become sufficiently resistant, the workman, by the aid of a long bar of iron, rolls it up in the form of a large ball, and then raises it on the top of the fuel, which he now thrusts down into the bottom of the furnace. Fresh charcoal is at the same time added, and the pressure of the blast so increased that the mass is again subjected to strongly oxidising influences, and a second time falls in a liquid state on the bottom of the hearth, where, from having now lost a considerable portion of its carbon, it soon forms into large spongy masses. The detached fragments are now collected with a long iron bar, and united in one mass. Should any portions appear to be imperfectly refined, they are again brought in a position to be directly acted on by the blast.

When the mass has become sufficiently refined, it is rolled into a large ball, and removed from the furnace by strong iron levers, by which it is first beaten to remove a certain portion of the adhering slag, and subsequently subjected to the action of a heavy hammer, by which the spongy matter is consolidated and welded together, whilst the pasty siliceous slag is at the same time expressed from its pores. During this operation the crucible is cleaned out, and the larger proportion of the slag which it contains drawn off; but a certain quantity of this substance is nevertheless retained in the furnace to assist in the decarburisation of the succeeding charge of cast iron. Before again proceeding to charge, it is frequently found necessary to cool the hearth by the introduction of water through the iron tube, q.

The slag thus removed is not, however, thrown away, but, together with the scale produced during the hammering of the mass, is preserved to be employed in the next operation during the first melting of the pig iron.

After being removed from the hearth, the loupe is transported by means of heavy tongs to an anvil, on which it receives the repeated blows of a heavy hammer, fig. 127, set in motion by a



127.

water-wheel, by which treatment the slag becomes completely expelled, and the iron consolidated into the form of a lengthened parallelogram.

The hammer head, H, commonly weighs from 800 to 1200 lbs., and is sometimes made of cast iron, although wrought iron is frequently employed, and in this case the hammer is provided with a face of hardened steel.

The anvil, A, is in most instances composed of cast iron, which, to give it greater solidity, rests on a heavy mass of the same metal, m, supported by a large wooden pile, b, firmly fixed in the



refinery floor. The wooden beam, h, which carries the hammer is strengthened by bands of iron, i j, and is supported by a strong cast iron ring, a, fig. 128, provided with trunnions, b, on which it turns when the head of the hammer is raised. These trunnions are sup-

ported by iron bearings fixed in the wooden supports. Parallel to the hammer-beam, and at a short distance from it, is situated a horizontal axle, B, moved by a water-wheel, and provided with a series of cams, c, which, by coming in contact with an iron band, situated at about one-third part of the distance from the head to the trunnion, forming the centre of suspension, first lift the hammer in the air, and then allow it to fall with its whole weight on the anvil, A, which is beneath it. To accelerate the fall of the hammer when lifted to its full height, it is made to come in contact with a long piece of elastic wood, which acts as a spring, and, by causing the rapid descent of the hammer, prevents the falling beam from coming in contact with the cam which is next in the series. The extreme range of the hammer, or the height to which it is raised from the anvil at each blow, varies from 2 feet to 2 feet 6 inches.

When the working of a piece of iron has been completed, the hammer is propped to the full height of its rise by a wooden support, which is removed as soon as the succeeding loupe has, by means of proper tongs, been placed on the anvil. At first the water-wheel is made to revolve very slowly, and consequently a considerable interval occurs between each blow of the hammer; but by degrees a more plentiful supply of water is admitted, and the hammer soon attains its maximum speed, which is continued to the end of the operation. Whilst the loupe is being worked on the anvil, it is so turned by the workmen that all its sides may successively become exposed to the hammer; and by this means the slag is rapidly expelled from the spongy metal, which is speedily formed into an elongated prism, of which the various parts have become firmly welded together. This is again subdivided, by a cutter, into three or four fragments or lopins, which are placed above the loupe formed in the next operation, and when sufficiently heated are drawn into bars, under a hammer especially adapted for that purpose. The mass is divided by a kind of knife, placed on it whilst under the large hammer, and which in its fall strikes the back of the cutter, which is thus made to divide the iron.

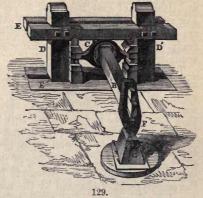
The hammer used for drawing the lopins into bars is in most instances much lighter, and makes a greater number of blows in a given time, than that employed for expressing the slag from the

## REFINING BY THE GERMAN FORGE.

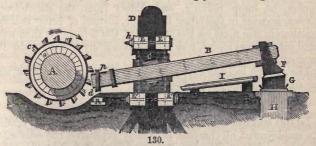
loupe when it first comes from the refinery. This hammer, which has much less lift than the one just described, is represented in figs. 129 and 130. In this case, instead of being raised directly by the cams, the motion is communicated on the other side of

the centre of suspension; the axle and cams, as in the other hammer, being turned by a water-wheel. Fig. 129 represents a front elevation, and fig. 130 a profile section of this hammer. A represents the axle of the water-wheel, on which are fixed the cams, c: these are fitted into a cast iron ring, which is firmly secured on the shaft by the wedges, a, made of hard wood.

The beam, B, carries the hammer, F, and is received



into a cast iron ring, c, which is provided with trunnions, working in bearings wedged between the perpendicular piles, D D', and the cross-bars, E E', which are strongly bolted together.



At the extremity of the beam opposite to that which carries the hammer, is placed an iron plate, p, which is firmly secured by means of the band d: against this plate the cams, which are turned in the direction of the arrow, are successively brought to bear, and by their pressure raise the hammer fixed on the other end of the wooden beam, which again falls as soon as the cam in contact with the plate p has so far depressed the end of the lever as to allow of its passing round without further impediment. The spring,  $\mathbf{R}$ , is in this case placed under the tail of the beam, instead of immediately above the head. The faces of the hammer, F, and of the anvil, G, are inclined at a certain angle with the floor: the guide, I, serves to steady long iron bars when worked under the hammer.

The weight of each loupe is in most instances about 2 cwts., and 100 lbs. of cast iron produce on an average 84 lbs. of bars. For every 100 lbs. of wrought iron obtained, 150 lbs. of charcoal are employed. The bellows are stopped as soon as the bloom is ready to be placed under the hammer, and the whole operation occupies about five hours.

The iron manufactured by this method is, unless the crude metal be extremely impure, of excellent quality, and good iron may, even in this case, be obtained, although at a considerable waste of fuel, and loss of metal. Refineries of this description have occasionally been supplied with heated air instead of the ordinary cold blast, but this having been proved to be of no value, except during the first fusion of the pigs, and also to cause great irregularity in the working of the furnace, it has now been universally discontinued. Attempts have been made to replace the employment of charcoal by the use of coke, but the iron produced by this means is so much inferior to that prepared with the usual fuel, as to more than compensate for the advantages derived by the substitution of the cheaper combustible.

The process above described is called by the Germans klumpfrischen, or lump refining, and differs from the durch-brechfrischen, because in the latter the loupe, instead of being rounded together in one mass on the hearth of the furnace, is then separated into several lopins, which are successively worked under the hammer.

The French call the first process the affinage au petit foyer, and the second, affinage par portions.

#### ENGLISH METHOD OF REFINING.

In this and other countries where the scarcity of wood renders the employment of charcoal extremely expensive, the conversion of cast iron into malleable metal is entirely effected by the use of pit coal or coke.

This transformation is produced by two consecutive operations, carried on in separate furnaces. In the first process the metal is melted in an apparatus in some respects resembling the old German refinery, as the liquid metal, after passing before the blast of numerous tuyeres, accumulates in the bottom of the crucible, from whence, instead of being allowed to remain until it has assumed a pasty consistency, it is run off into a flat mould, prepared for that purpose, a little beneath the level of the hearth. By this treatment the metal loses a considerable portion of its carbon, and nearly the whole of its silicium, and is thereby rendered extremely hard and brittle, its surface being usually covered with numerous small blisters, like those observed in some varieties of steel, to which its composition is made in some degree to approach. The iron in this state is known by the name of fine metal, and is now transferred to another furnace, in which its decarburisation is completed. The apparatus in which this process is carried on consists of a reverberatory furnace, in which, after being again fused, it is subjected at a very high temperature to a current of atmospheric air, by which its surface is partially oxidised, and its combined carbon eliminated in the form of carbonic acid gas. During this operation a portion of the oxide formed combines with the silica resulting from the oxidation of the small quantity of silicium still remaining in the fine metal, and forms a basic slag, which reacts on the carbon contained in the metal.

As, however, the quantity thus produced is very inconsiderable, it is usual to throw into the furnace a certain amount of rich slags obtained during other stages of the manufacture. The oxide of iron contained in these scoriæ now reacts on the carbon still retained by the metal, which, from the escape of carbonic oxide gas, shortly appears to boil; and this, on reaching the surface, burns with a pale blue flame, and is thus converted into carbonic acid.

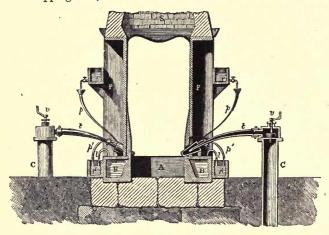
When the metal is judged to be sufficiently refined, the workman collects it together in the form of large balls, similar to the loupes of the German forge, and exposes them successively to the action of a heavy hammer, by which the vitreous slag is expelled, and the spongy metal compressed into a compact form. The operation by which the last portions of carbon are extracted from the metal, is called *puddling*, and the puddled iron, after being properly compressed by the heavy hammer above mentioned, is again heated, and then passed through a series of rollers, by which it is formed into bars of greater or less length and diameter.

The *fine metal* of the English process very nearly corresponds to the iron of the *petit foyer* after it has undergone the first fusion, and the puddled balls, when collected on the furnace bottom, correspond to the rounded loupe when ready for carrying to the hammer.

The Refinery.—The English fining furnace, or refinery, is commonly built on a mass of brick-work about 9 feet square, which is raised but little above the level of the floor, and placed either in a shed or in the open air.

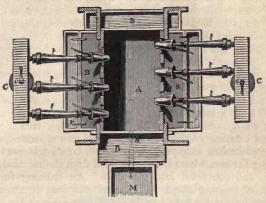
The fire-place consists of an irregularly-formed hearth,  $\Lambda$ , figs. 131 and 132, 2½ feet in width, and 3½ feet in length, composed of

four cast iron troughs, B, through which a current of cold water is constantly passed to prevent their fusion by the heat developed in the furnace. The bottom of the crucible is formed either of gritstone or argillaceous sand, and is slightly inclined in the direction of the tapping-hole, h.



131.

The air is supplied by the blowing cylinders which supply the blast furnace, and enters the hearth through the six tuyeres,  $t_{i}$ so arranged that the current issuing from those on the opposite sides of the crucible are not disposed in the same plane. These tuyeres, like those in the furnaces in which cast iron is prepared, are provided with double casings, and through these a current of cold water is constantly flowing. The water for this purpose is furnished by the reservoirs r, from whence it is supplied to the tuyeres through the pipes p, and afterwards escapes through the tubes p' into the tanks r', into which the water from the spaces B also flows through the pipes l. Each of these furnaces consumes about 400 cubic feet of air per minute; this enters through the pipes c, furnished with screw valves at v, by which the quantity passing through the nozzles is easily regulated. The tuyeres are inclined at an angle of from 25° to 30°, and are so placed that their axes intersect the opposite faces of the crucible a little above the angle formed by its junction with the bottom of the furnace. The hearth is surmounted by a chimney, s, of from 16 to 18 feet in height, supported by four cast iron columns, P, which admit of free access to the fire on all its sides. The tapping-hole, h, fig. 132, is placed in one of the shorter sides of the hearth, and by it the melted metal, together with the slag, flows out on the mould, M, where it is subsequently cooled by the addition of water. The plate of fine metal thus formed is about 10 feet in length,  $2\frac{1}{2}$  feet in breadth, and 2 inches in thickness. A portion of the slag forms a thin crust over the surface of the iron run out, but the greater part is collected in a small pit made for that purpose at the lower end of the mould.



132.

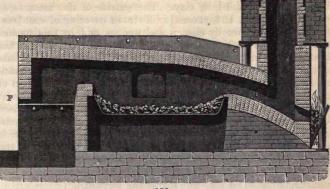
The working of the English refinery, like that of the German forge, is continuous, so that as soon as one charge of metal is run out, the hearth is again prepared for the reception of a fresh supply. Immediately after tapping the fine metal into the mould, M, the workman detaches, by means of a long iron bar, any portions which may remain adhering to the sides of the furnace, and the ignited fuel being pressed down into the bottom of the crucible, new coke is added until the hearth has been filled to a proper height. The pigs of iron are now placed symmetrically on the top of the coke, taking care to cover the whole surface, and at the same time allowing sufficient vent between them for the escape of the smoke and gases produced. Each charge of the finery ordinarily consists of six pigs, of which four are laid parallel to the sides of the furnace, and on these the two others are made to rest transversely. The weight operated on at one time varies from 1 ton to 30 cwts. This quantity occupies about two hours in refining, and loses from 13 to 17 per cent. of its weight during the operation. At the expiration of a quarter of an hour after charging, the iron begins to melt, and passing drop by drop through

the air furnished by the tuyeres, gradually accumulates at the bottom of the hearth. By this means a portion of the metal becomes oxidised, and uniting with the siliceous cinder contained in the fuel, as also with the silica resulting from the oxidation of the silicium present in the cast iron, forms a fusible vitreous slag. This slag, which is extremely rich in oxide of iron, exercises a strong decarburising action on the iron on which it floats, and in order that these changes may be properly effected, the air from the different tuyeres is allowed to play on the surface of the fused mass for a considerable time after the whole of the iron has been collected at the bottom of the crucible. During this period the fuel is observed to be continually lifted by the motion caused in the metal by the escape of the gaseous oxide of carbon produced by the reaction of the rich silicate of iron constituting the slag. When in this state, the metal is not stirred, as in the German refinery, but as soon as the decarburisation is judged sufficiently advanced, the tap-hole, h, is opened, and the contents of the hearth allowed to flow into the mould, M, where it is cooled by the addition of a large quantity of cold water, by which treatment it is rendered extremely brittle. The slags are now separated, and the fine metal broken into pieces convenient for its transport to the puddling furnace, where it is to be freed from the remainder of its carbon, and converted into soft iron. An ordinary furnace is capable of refining about ten tons of cast iron in twenty-four hours, and consumes from 4 to 5 cwts. of coke for each ton of metal refined. The fine metal, besides containing less carbon than the pig iron from which it was prepared, has also lost nearly the whole of its silicium, as well as various other impurities which pass off in the form of slag. From the impurities contained in the fuel, iron refined by the aid of coke is found to be less pure and tenacious than that in the preparation of which charcoal alone has been employed, and for this reason the latter fuel is constantly used when metal of a peculiarly good quality is required. The iron from which tin plates are manufactured is therefore refined with charcoal, but as in this case the metal accumulates on the sides of the furnace in the form of clots or lumps, they are directly removed from the refinery hearth to the tilt hammer, and flattened into thin plates before being removed to the furnace, in which their treatment is completed.

The Puddling Furnace.—The further purification or puddling of iron is effected in a reverberatory furnace, figs. 133 and 134, of which the first is a vertical section, and the second a ground plan. The hearth, A, which is composed either of fire-brick set on edge, or of a plate of cast iron covered with a layer of slag, is laid very nearly level, but has nevertheless a slight inclination towards B,

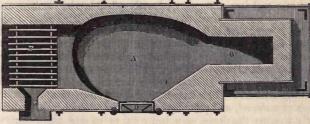
#### PUDDLING.

where the fall becomes considerable, and at the lowest point of which is situated the floss-hole, h, for the removal of the slags which accumulate in the furnace during the process of decarburis-



133.

ation. The hearth, which is usually 4 feet in width at the widest part, is reduced to about 1 foot 8 inches at its other extremity,



134.

and has in most instances a length of about 6 feet. This part of the furnace is separated from the fire-place, F, by a bridge 10 inches in height, and one brick in thickness. The fire-bars are made moveable for the greater convenience of removing the clinker, and cover a space having for its length the width of the hearth next the bridge, whilst it measures, according to the size of the furnace, from 2 feet 8 inches to 3 feet 4 inches in the other direction. The draught through the apparatus is determined by a chimney composed of bricks strengthened by numerous iron ties, and varies from 30 to 50 feet in height. The upper part of this shaft is furnished with a sheet-iron damper, opened by a chain and lever,

by which the workman can regulate at will the amount of air passing through the furnace. The walls of this arrangement are built of ordinary masonry, but the dome and all the other parts exposed to a high temperature are exclusively constructed of good firebricks, closely bedded in clay. The outside of the mass is, as represented in fig. 134, encased in a strong covering of cast iron, firmly held together by clamps and wedges, and by this means, not only is the perfect solidity of the structure ensured, but the inconvenience attending the entrance of cold air through the clefts of the brick-work is entirely avoided. The door, E, is in communication with the grate, and closed either by an accumulation of coal used for fuel, or by sliding doors raised by a chain and lever. In this country the feeding-hole of the furnace is usually closed by the accumulation of coal only. The opening, D, fig. 134, communicates with the hearth or sole of the furnace. This door is chiefly used for working the metal with an iron bar during the process of puddling, and is closed by an iron frame filled with fire-bricks, and raised by a chain and lever. Another aperture, sometimes placed on the same sole of the furnace, but considerably nearer the chimney, is employed for charging the refined metal and cleaning out the apparatus at the close of each operation, and is therefore kept closed by an iron plate during the working of the charge. The hearth, as before stated, is frequently composed of a cast iron plate covered with a fusible slag, and in this case a space for the circulation of cold air is left between it and the brick-work: by this means the temperature to which it is exposed is constantly kept lower than the point of its fusion, and the plate consequently remains uninjured under circumstances by which it would otherwise become rapidly destroyed.

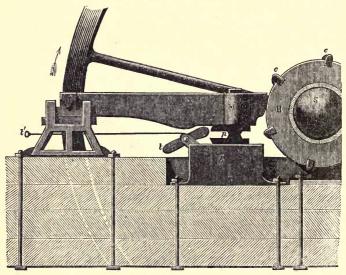
The puddling of fine metal in this furnace is conducted in the following manner:-The iron is introduced into the furnace by means of a shovel, and piled up on the sides of the hearth until it nearly touches the dome, care being taken to keep the centre of the sole clear for working the charge, as also to allow the heated air to circulate freely around the broken fragments. To the broken metal a portion of rich slag and iron scales is afterwards added. The doors are now closed, fresh fuel is thrown on the grate, and the damper at the top of the chimney entirely closed. At the expiration of about half an hour the sharp edges of the fine metal begin to melt, and flow on the bottom of the hearth. The workman at this stage removes a small iron plate, by which an opening in the working door is closed during the first part of the operation, and with an iron rod stirs the melted portions of metal in order to expose new surfaces to the action of the oxidising gases passing through the furnace; he also removes it to a certain dis-

tance from the bridge, to prevent its running together in one mass. When the whole of the charge has been thus reduced to a pasty state, the fire is lowered, the damper gradually closed, and, if it be found necessary, a little water may be thrown into the furnace. The metallic bath now appears to boil, from the evolution of carbonic oxide gas, which immediately takes fire on reaching the surface, and burns with a blue flame. The puddler now keeps the metal constantly stirred with an iron tool called a paddle, thus continually exposing fresh surfaces to the action of the gases in the furnace. It is, however, desirable that the metal should be subjected as little as possible to the direct action of atmospheric air, by which it would become rapidly oxidised; and for this reason the working door is not opened more than is absolutely necessary for carrying on the work. After a time the metal begins to lose its coherence, and becomes sandy, or, as the workman expresses it, dry. The evolution of oxide of carbon now rapidly declines, and soon ceases altogether; but the stirring of the mass is continued until it has assumed a uniform granular appearance. When this point has been attained, the fire is again forced, and the damper gradually raised: this causes the sandy particles to agglutinate and offer considerable resistance to the paddle. The iron is now said to work heavily, and a portion of the scoria is run off through the floss-hole left for that purpose at the end of the furnace farthest removed from the bridge. It now only remains for the workman to form the iron into balls, and this he does by attaching a small portion to the end of his paddle, and so rolling it in the hearth as to collect other fragments, which become firmly welded to it. In this way the whole of the charge is collected into lumps weighing from 60 to 70 pounds each, and these, when formed, are placed by a kind of rake called a dolly, and which is heated to redness before being used, in the hottest part of the furnace, where they are pressed for the purpose of squeezing out the slag contained in the spongy mass. This making of the balls occupies about twenty minutes, and when it is accomplished the doors are closed for a short time, and the dampers opened for the purpose of welding the particles of the metal closely together. The loupes are now successively removed from the furnace, and placed either under the hammer or squeezer, in which case they are often welded to a long iron rod, which serves the workman in lieu of a handle. When, on the contrary, as in most parts of Wales, they are passed directly to the roughing rollers, they are lifted directly from the hearth by the help of heavy tongs only.

The charge of a puddling furnace is usually from  $3\frac{1}{2}$  to 5 cwts. of fine metal. When very pure cast iron, such as that prepared from charcoal, is to be treated, the preliminary operation of refining is

sometimes dispensed with, but for ordinary rough metal its previous purification is almost indispensable. Each furnace receives from 10 to 11 charges in the course of twenty-four hours, and the average loss experienced by the fine metal may be estimated at about 9 per cent. on the quantity treated. About five puddling furnaces are required for each finery, and every charge of metal puddled requires the combustion of just its own weight of coals. The operation may be divided into four distinct periods. The melting of the refined metal commonly begins to take place at the expiration of twenty or twenty-five minutes. At the end of an hour and a-half the charge is completely reduced to a sandy state. It is in this state kept heated for another half-hour, and at the expiration of that period the balling is commenced, and this occupies about the same length of time.

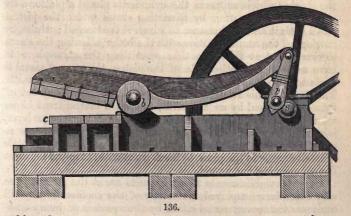
Compressing the Puddled Balls.—The hammer employed for compressing the balls after their removal from the puddling furnace, is commonly made of cast iron, and is represented in fig. 135. The weight of the helve, M, varies from 3½ to 4 tons, and its length is in most instances about 10 feet.



135.

The axis, *a*, of the hammer rests on heavy plummer-blocks, firmly secured by strong bolts passing through a large mass of masonry, on which one or more courses of wooden beams are placed for the purpose of affording a certain degree of elasticity to the arrangement. The head, p, is made of wrought iron, faced with steel, and weighs from 7 to 8 cwts. This is attached to the helve by passing through a large hole cast in its extremity, and is firmly secured by iron or wooden wedges. The anvil, like the hammer, is composed of two parts: one of these, called the pane of the anvil, is, like that of the hammer, formed into a series of grooves for the purpose of better expressing the slags from the balls, and welding their particles more closely together. This is of equal weight to the head of the hammer, and rests on a large cube of cast iron, to which it is secured by proper wedges. The weight and dimensions of the iron block, b, supporting this face, vary in different manufactories, but on an average it may weigh about 4 tons, although six-feet cubes of cast iron have been sometimes employed for this purpose. The head, which lifts from 16 to 24 inches, and makes from 75 to 100 blows in a minute, is raised by a succession of cams, c, fixed in a heavy cast iron collar, H, called the cam-ring-bag, which may be 3 feet in diameter, and 18 or 20 inches in thickness : this weighs from 4 to 41 tons, and is firmly keyed to a powerful shaft, s, moved either by steam power or a water-wheel. The apparatus t t is for the purpose of propping up the head of the hammer when not in use. The puddled loupes are held under this instrument by an iron rod called a porter, and, when the slag has been sufficiently expressed, they are passed through a series of grooved iron rollers.

The heavy iron hammer is now sometimes replaced by a kind of hinged press, fig. 136, in which the balls of puddled metal are



subjected to considerable pressure by means of a powerful lever.

This apparatus consists of two strong jaws, a, b, c, joined together at b like a pair of common scissors: in this case the cutting edges are, however, replaced by plane surfaces, in which are numerous latitudinal grooves, in order to retain the loupes of metal to be operated on. The lower jaw, c, consists of a cast iron box, through which a current of water constantly flows, in order to prevent its becoming too highly heated by the masses of hot metal which it supports.

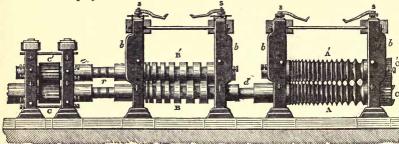
The upper jaw, a, receives its motion from the shaft, s, with which it is connected by the crank, t, and which must be made of stout wrought iron of good quality. This press occasions less waste than the ordinary hammer, and at the same time more expeditiously fits the loupe for passing through the rolling mills. Both these contrivances have, however, of late years become very generally superseded by Nasmyth's steam hammer, which is equally applicable to the compression of the puddled loupes and the forging of large masses of finished iron in the manufacture of anchors and other heavy articles. The head of this instrument consists of a cast iron block, to which is fitted a steeled wrought iron facing. To lift this weight, which frequently amounts to from four to five tons, it is attached to a rod connected with a piston working in a steam cylinder, which is supported at a convenient height on a stout stand of cast iron. The sides of this frame are also grooved so as to form guides for the hammer head. The anvil is placed between the uprights which support the cylinder, and is provided with a steeled facing similar to that of the moveable mass constituting the hammer itself. On the top of the staging which supports the cylinder is placed a platform for the hammer-man, who, by admitting steam under the piston, raises both it and the hammer to which it is attached; whilst, by cutting off the communication with the boiler, allowing the steam to escape, and at the same time permitting the atmosphere to have access to the other side of the piston, the mass of metal is made to fall with its whole weight on the anvil which is beneath. The steam in this arrangement is alternately admitted and cut off by a slide worked by an eccentric; but when intermittent blows are to be applied, the slide, which is connected to a proper lever, is worked by hand. The workmen, by long practice, become so completely masters of this machine as to be able to cork a bottle without danger to the glass, or break a nut without in the slightest degree crushing the kernel.

In large establishments these hammers are at the present time very extensively employed, but many of the smaller forges still compress the spongy metal either by the squeezer or heavy castiron hammer raised by the head.

The cylinders by which the soft metal is compressed, and afterwards drawn into bars, are of two distinct kinds. The first, which are called *puddling rolls*, serve to compress and weld together the balls of metal after they are removed from under the hammer, although in some localities, and particularly in Wales, they are passed through the rollers as soon as they have been removed from the furnace. The second kind is employed exclusively for the purpose of extending into bars the masses of puddled iron after they have been cut into short lengths and rewelded to improve their quality : these are known by the name of rollers, and are differently grooved according to the pattern of the bars they are intended to produce. These cylinders are fixed in pairs, one above the other, in a heavy framework of cast iron, and are so connected by strong toothed wheels as to turn in contrary directions. Motion is communicated to the shafts either by steam or water power, and the distance between the two cylinders admits of being easily regulated by screws acting on the bearings in which the trunnions are made to work. A narrow oblong foss runs beneath the frame in which the rollers are placed: through this a stream of water is continually made to flow, and in it is collected the scales which fall from the surface of the heated iron when passing between the cylinders. The sides of this rectangular pit are commonly composed of large blocks of stone resting on a solid mass of masonry, into which are built strong beams either of wood or cast iron, to which the uprights or housing frames supporting the rollers are firmly secured. A small stream of water is occasionally conducted by a pipe to each pair of cylinders, which are thus kept cool, and prevented from being injured by the hot metal passed between them.

The roughing rolls are usually 5 feet in the clear between the bearers, and 18 inches in diameter: the trunnions are turned out of the same piece of metal, and are each about a foot in length. Each of these rollers has a series of from five to seven regularly decreasing grooves of an elliptical form, so arranged that the shorter axis of the figure formed by the meeting of the corresponding grooves in the two cylinders is equal to the longer axis of the ellipse formed by the junction of the two grooves which come next in succession. The smaller axis of each ellipse is also invariably perpendicular to the surfaces of the two cylinders by the meeting of which it is formed; and, for this reason, every bar which has passed between the rollers is made to make a quarter revolution before it enters the grooves which come next in the series, and is thus equally compressed and drawn out in all its parts.

The roughing and preparing grooves are sometimes contained on the same cylinders, but are more frequently arranged on distinct rollers, as in fig. 137, where A A' represent the roughing rolls, and B B' those by which the metal is formed into flattened bars, to be subsequently faggoted and drawn into iron of any required size. The first three or four grooves of the roughing rollers are also commonly provided with asperities somewhat resembling the teeth of a file, which take firm hold of the mass of metal presented before the opening, and draw it through without danger of the slipping which would occur if smooth surfaces only were employed.



137.

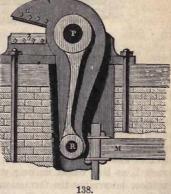
To support the balls and masses of metal which are to be passed through the rollers, a thick plate of cast iron, notched on the edge so as to admit of being closely applied to the cylinder, is placed on a level with the bottom of the notches on the lower roll. This piece is called the *apron*, and rests on iron bars stretched between two consecutive standards of the housing frame. These uprights vary from 5 to 6 feet in height, and are usually about 2 inches thicker perpendicularly to the faces of the rolls than parallel to their surfaces, in which direction they measure from 10 to 11 inches. The different bearers, *b*, are connected together at their upper extremities by stout iron bars, drawn tight by screw-nuts: these are used by the workmen to support the heavy tongs employed in lifting the masses of hot iron to be rolled into bars.

The distances between the rollers are regulated by the screws, s, and the connections between them established by means of the strong toothed wheels, c c', by which they are made to revolve in opposite directions. The two series of rolls are united by heavy couplings, d, r, tightly keyed together.

Puddled iron which has been rolled into bars immediately on its removal from under the hammer is always of very inferior quality, being extremely hard and brittle, besides being subject to numerous flaws and imperfections not observed in ordinary bar iron. This hardness of the metal is, however, in certain instances found advantageous, and for this reason the bars of iron laid down on our railways are often composed of coarse hard iron, which is made to assume its peculiar shape by being rolled between cylinders having on their surfaces grooves so arranged as to form the profile of the rail wanted. When, on the contrary, the iron is required for ordinary purposes, and should consequently be possessed of tolerable tenacity, its quality is improved by cutting the rough bars into short lengths, and afterwards welding them together in bundles, and again passing them through a set of rollers, the grooves of which correspond in size and form to the dimensions of the bars or rods to be produced.

To effect this, the bars of puddled iron are, by means of powerful scissors, fig. 138, cut into lengths of about a foot each, and subsequently heated to the welding point in an oven expressly adapted for that purpose, and called a *mill furnace*.

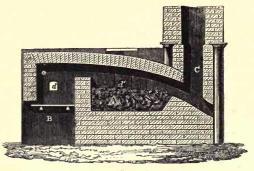
These shears are composed of two jaws terminated by cutting edges, a b, made of hardened steel, and firmly bolted to the iron limbs to which they are attached. The lower blade, b, is immoveably fixed to a cast iron stancheon, whilst the upper one, marked a, moves on the pin, P, passing through the same support. To the upper limb, b, of the instrument is attached the lever, P B, which, being connected with the rod, B M, attached by a crank to the shaft



of the steam-engine, causes the jaws of the shears to alternately open and shut at every revolution of the axle by which the power is supplied. In this way motion is given to the scissors, which easily divide bars of iron an inch or more in thickness when placed between the jaws.

The iron thus cut into short lengths is made into heaps or *piles* proportionate to the size of the bars to be manufactured, and heated in a furnace of which fig. 139, next page, represents a vertical section. This apparatus differs chiefly from the puddling furnace in the relation existing between the hearth, A, and the grate, **B**, which in the latter is made much larger than in the former, on account of the greater heat which is in that case required. In this furnace also there are two doors, by one of which, *d*, the fuel is introduced into the fire-place; whilst the other, which is not seen in the woodcut, is situated under a chimney, and is employed for introducing the bundles of iron

into the hearth, A, and removing them when sufficiently heated to be passed through the rollers by which they are to be drawn into



139.

bars. This latter opening is closed by a kind of damper, which is worked by a lever.

It is of the greatest importance in furnaces of this description that no air be allowed to enter but that which has lost the greater portion of its oxygen by having first passed through the grate, and for this reason it is essential that the doors should remain completely closed during the time that the faggots of puddled iron are being heated. If this precaution were not attended to, a considerable loss would be sustained by the oxidation of the metal treated, as this oxide, uniting with the siliceous matter of the furnace, determines the formation of large quantities of rich slag at the expense of the metallic iron. It is also to be observed that the large door is so placed beneath the chimney that the air which would otherwise enter the furnace on the withdrawal of the damper makes its way directly to the flue. When the piles of puddled iron placed on the sole, d', have acquired the temperature necessary for welding them together, they are successively removed through the door, and passed between the finishing rollers until they have assumed the required form and dimensions. These rolls are turned with greater precision, and adjusted with more accuracy, than is required in the first set, as it is essential that the finished bars should have a regular form, and be perfectly smooth on the surface. They are also made to turn with more rapidity than the roughing rolls, to prevent the iron from becoming chilled before it has time to pass through them. The quickness of this motion depends, therefore, in a great measure on the thickness of the bars to be produced, as the smaller specimens will evidently soonest become cold. For this reason, where very small iron is manufactured, it is usual to employ a series of three rollers placed one above the other. In this case the motion is directly communicated from the engine or water-wheel to the middle cylinder, which being connected by cog-wheels with the other rollers placed above and beneath it, causes them to revolve in contrary directions. These cylinders make, on an average, from 150 to 200 revolutions per minute. To use them, the heated bar is first passed between the first and second rolls, and then returned from the other side between the set formed by the second and third.

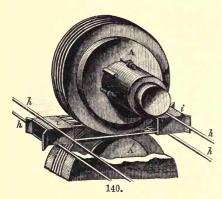
Manufacture of Sheet Iron.—Sheet iron is made either by hammering the heated metal to the proper thickness by the same methods that in some localities are still employed for the purpose of drawing it into bars, or it is made to acquire the proper form and thickness by being passed, when strongly heated, between smooth rollers with polished faces arranged in the same manner as those intended for reducing it into bars.

Two sets of cylinders are employed for this manufacture: by the one, the metal is roughed into something like the required dimensions; and by the second, which only differs from the other in being turned perfectly smooth, and more accurately adjusted, the sheets are finished off, and are given an even and polished surface. The metal employed for making sheet iron ought to be very soft and tough; and when thin sheets are required, such as those of which tin-plate is manufactured, the best charcoalprepared iron only can be used.

To give to the metal the form of sheets, it is first drawn out into flattened bars of a greater or less thickness according to the dimensions and solidity of the plates to be manufactured. These are afterwards cut by powerful shears into lengths corresponding to the width of the sheets which it is wished to prepare. This is usually done immediately after the metal has passed through the preparing rollers, and whilst it is still hot. The prepared masses are now introduced into a reverberatory furnace, where they are heated to redness, and, when sufficiently hot, are passed through the roughing rolls in such a way that the length of the bars may be parallel to the axes of the cylinders between which they are compressed. The plates are in this way acted on by the rolls two or three successive times, the distance between them being slightly lessened at each operation for the purpose of thinning the sheet by the continuance of the pressure exerted on it by the cylinders. The roughed plates are now a second time reheated in a reverberatory furnace, but not in that employed for softening the rough bars before passing through the preparing rolls, which, although very similar to the one now used, is kept entirely for the service of the roughing rolls alone. Great precautions are necessary to prevent the entrance into the furnaces of any atmospheric air which has not passed immediately through the fire-grate, as the flattened masses of iron would become externally oxidised, and could not afterwards be made to acquire the necessary smoothness of surface. The heated plates, after being passed through the finishing cylinders, are at length found to have assumed the required thickness and dimensions, and are subsequently beaten with wooden mallets for the purpose of removing the scales of oxide which in greater or less quantity are invariably attached to their surfaces.

When the iron has been rolled into very thin sheets, such as those employed in the manufacture of tin-plate, the smoothing of the surface is effected by a distinct and separate operation. For this purpose the reduced metal, after being heated to redness, in order to restore its softness, is laid in successive layers on a smoothly polished surface of cast iron, where it is strongly compressed by the descent of another surface acted on by hydraulic pressure.

For the production of small square iron bars, such as those from which nails are commonly made, a system of rollers is employed, which have received the name of *slitters*, fig. 140. The



ridges of these, instead of being obtuse and exactly meeting each other, as in the case of ordinary rolling cylinders, are composed of sharp steel discs, of an annular form, and which enter into opposite grooves of about two inches and a-half in depth; so that any piece of sheet iron which may be passed between them is immediately divided into a series of slips corresponding in number to

the circular cutters of the apparatus. These slitters, AA', are composed of steel plates, so arranged on a heavy cast iron shaft as to fit tightly between those placed on the opposite rollers, and all strongly secured in their place by stout iron caps and screw bolts. The metallic sheet of proper width and thickness is steadied whilst passing between the knives by the guides, ii, and the tension rods, h, which keep the cut bars separate whilst passing out on the opposite side of the arrangement. The wrought iron bars, h, are secured to the uprights of the housing frame, and serve to secure the guide and its appurtenances in a proper position.

## MANUFACTURE OF IRON BY THE CATALAN OR FRENCH METHOD.

In the French Pyrenees, Corsica, and in some provinces of Spain, instead of manufacturing malleable iron by treating cast iron in a refinery and puddling furnace, it is obtained by one operation directly from the ore. In order that this branch of industry should be advantageously carried on, it is necessary that the ores treated be not only extremely rich, but also very fusible, and that charcoal, which is the fuel employed, be obtained at a low price, since every ton of bar iron thus produced will require in its preparation the expenditure of rather more than three times that weight of fuel.

The Catalan furnace consists of a quadrangular crucible, composed of refractory masonry, and attached like an ordinary smithy fire-place to one of the walls of the workshop in which it is situated. Three distinct modifications of this smelting hearth are used on different parts of the Continent, under the names of Catalan, Navarrese and Biscayan forges, but as in principle these exactly resemble each other, it will be sufficient to describe in detail the *Catalan forge*, which is that most extensively employed.

The hearth of this furnace is established in a large mass of stone-work, cemented together with refractory clay, and which, instead of being built directly on the floor of the foundry, is supported on one or more small arches, to admit of the escape of moisture, and to preserve the bottom of the crucible from being injured by any dampness which might otherwise find its way into the masonry. On the top of these arches is arranged a layer of fire-clay and iron slag, which is well beaten down, and supports a large block of compact granite, which forms the bottom of the crucible, and on this are placed the four sides of the hearth, a, b, c, d, as shown in figs. 141 and 142.

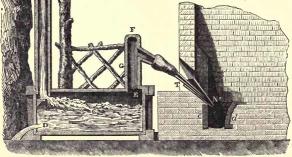
The face, a, which is of iron, is called the *chio*, and from this side of the furnace the liquid slags are run off through a hole left for that purpose. That opposite is called the *cave*, and is entirely composed of masonry held together by refractory clay. This side is somewhat curved in an outward direction, and is slightly inclined from the bottom towards the top.

The side of the furnace, c, on the left of the sketch, is called the *porges*, and is composed of heavy bars of iron placed one above the other, so as to form a kind of vertical wall. The other side of the furnace, d, opposite the tuyere, is known by the name of the *ore*, or *contrevent*, and is composed of pieces of iron, having a wedge-shaped section, and so arranged as to form a rounded surface, with its convex side placed towards the fire. The nozzle, N, by

which the wind is brought into the hearth, has the form of a truncated cone, and is made by turning a piece of sheet copper into the proper form, without soldering its edges. This nozzle rests on the upper plate of the porges, and encloses the tuyere,  $\tau$ ,

by which the furnace is supplied with air, by a water blowing machine, represented in figs. 141, 142, and which is connected to the tuyere by a leathern hose. The amount of inclination given to the nozzle is found to materially affect the working of the furnace, and is made a great mystery of by the workmen employed. In most instances, however, the tuyere makes an angle of from  $35^{\circ}$  to  $40^{\circ}$  with the bottom of the hearth.

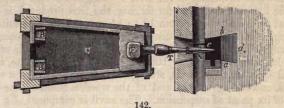
The dimensions most commonly employed for the Catalan furnace are as follow: length of the hearth from the porges to the contrevent at its widest part, 3 feet; width of the crucible, from the chio to the face of the cave, 1 foot 9 inches; total depth, from the surface to the bottom of the



141.

hearth, 2 feet 2 inches. The distance between the porges and the contrevent, at its narrowest part, is usually about 27 inches.

These forges are invariably placed on the declivity of a hill, and are supplied with air by a water blowing machine, called a *trompe*. This apparatus consists of a large eistern, A, which is supplied with a constant stream of water, and connected with the box, c, by two wooden pipes, B, B', about 20 feet in length.



The lower case, C, which is secured on all sides, and closely united to the tubes B, B', is pierced with two openings, the one, D, near the bottom for the escape of the water, and another in the lid, at E, through which the air escapes into the furnace through the tube G, F, T, N.

The openings of the tubes B, B', are at their point of junction with the reservoir partially closed by a sort of wooden funnel, which causes the water to descend in the middle portions of the upright pipes, instead of adhering to and running over their inner surfaces, as it would be otherwise liable to do. A little beneath the openings of these funnels, called the *étranguillons*, four small openings, g, are cut in an inclined direction through each tube; these are called the *aspirateurs*, and serve for the passage of the air drawn into the apparatus by the downward motion of the streams of water. The two upright columns, B, B', are firmly secured into the lid of the lower case, c, and are placed immediately over, and a short distance above a small wooden shelf, on which the descending currents of water are by their fall broken into foam.

The action of the apparatus may be explained as follows: the water flowing from the upper basin, A, draws down with it a current of air, which enters through the holes, g, in the vertical pipes, and passes into the lower cistern, c. The water which is broken by its fall on the bench, escapes by the opening D, whilst the air which has been drawn with it into the lower box, escapes by the aperture E. The position of the boards constituing the étranguillons is easily regulated by means of wedges, which allow of the descent of a larger or smaller supply of water, according to the requirements of the trompe. In order during the working of the machine to regulate the amount of air passing into the furnace at the different stages of the operation, each of the descending columns, B, B', is provided with a plug, suspended by a lever and iron rod, and by means of which the current of water, and conse-

quently that of air also, is readily controlled by the workmen, without having occasion to leave the workshop, into which a chain attached to the other extremity of the lever is brought for that purpose.

The hammer employed for forging the iron produced, is made of cast iron, and weighs from 12 to 14 cwts. This is mounted on a long wooden beam, frequently made of beech, and bound, for the sake of imparting to it solidity, with numerous bands of iron. The hammer makes from 100 to 125 blows per minute, and is raised by a series of cams, arranged around the axle of a waterwheel, and acting on the end of the wooden beam on the other side of its point of suspension. The anvil is composed of a block of iron, fastened by a tenon, on a large mass of cast iron, which is itself securely bedded either on a wooden pile or heavy block of stone, sunk beneath the floor of the foundry.

In order to understand the method of working this forge, let us suppose that a mass of iron or loupe has been just extracted from the furnace, and that the workmen are ready to clean out the hearth for the purpose of commencing another operation.

To do this they first remove from the crucible the burning charcoal which it contains, and then carefully scrape off from the sides any portions of scoriæ, or other fused matter, which may be adhering to them. They now again throw a supply of burning charcoal into the hearth, which they subsequently fill with this combustible up to the level of the tuyere. The hearth is now divided either by a shovel, or piece of sheet iron, into two compartments parallel to the face of the porges, and in such a way that the distance between the porges and the shovel may be twice as great as that comprised between it and the contrevent. Charcoal is now added in the space between the shovel and the tuyere, and



on the opposite side is piled the roasted mineral, reduced to pieces about the size of eggs. The shovel is successively raised in proportion as the space is filled up, and in this way a saddle-backed heap, a, b, c, fig. 143, is raised against the contrevent, which is terminated in one direction by the side called the chio, and the other by the face of the cave. The surface, a b, is now slightly covered with damp charcoal powder, and the space, A, between the heap of mineral and the porges, entirely filled up with fresh charcoal, in moderately sized pieces.

When the furnace has been thus prepared, the trompe is set in action, and the air admitted into the hearth. This is at first done

with considerable caution, but the blast is progressively increased, until it is allowed to play into the hearth at its full pressure. Whilst this is going onwards, the heap of broken ore is gradually roasted and reduced, and the workmen, taking advantage of this opportunity, forge into bars the mass of iron produced by a former operation, and which for this purpose is commonly divided into four separate pieces, or *massouquettes*. These fragments are placed in the midst of the mass of charcoal lying between the heap of ore to be wrought and the nozzle of the tuyere, which furnishes the air necessary for carrying on the combustion of the fuel, and, after being duly heated, are placed under the hammer, by which they are made to assume the required form.

As the operation advances, and the fuel is consumed, fresh charcoal is added to supply its place, and the powdered mineral obtained by sifting the ore as it comes from the mine is slightly sprinkled over the surface of the fire. These siftings, which are called *greillade*, are slightly moistened with water, after being thrown on the hearth, as they would otherwise be liable to be blown away by the force of the blast, and have a tendency to pass too rapidly towards the bottom of the crucible, through the interstices occurring between the fragments of the fuel.

The charcoal in the immediate neighbourhood of the tuyere, and on which the full action of the blast is made to play, becomes rapidly consumed, with the formation of carbonic acid gas, which escaping through the surrounding charcoal heated to redness, is soon reduced to the state of carbonic oxide. This, from the construction of the furnace, has to pass through the openings left between the lumps of mineral, before finding its way into the open air; and the mineral which has now lost all traces of its volatile constituents, and is very strongly heated, is in a great measure reduced by this means to the state of spongy metallic iron, while the oxide of carbon is at the same time converted into carbonic acid gas, and escapes in that form into the atmosphere. Another portion of the oxide of iron present, instead of being obtained in the metallic state, merely becomes converted into protoxide, which, uniting with the siliceous matters of the charge, gives rise to a large quantity of very fluid scoria or slag, which accumulates on the bottom of the hearth, and is occasionally drawn off by the hole left for that purpose in the face of the furnace, called the chio.

At the expiration of two hours from the commencement of the operation, the full blast of the blowing machine is admitted into the furnace, and the greillade, which constantly descends with the fuel, begins to furnish a certain quantity of slag and spongy iron, which accumulates at the bottom of the crucible. At this stage of the process, the founder begins to prepare for the formation of

the mass or bloom, and, by passing an iron bar between the contrevent and roasted mineral, pushes forward those portions of it which he judges to be in the most forward state, in the direction of the nozzle by which the air is admitted. Fresh additions of charcoal and greillade are also successively made during the whole time of the operation, and at the expiration of about five hours from the time of its commencement, the entire charge has reached the bottom of the furnace, where the spongy iron is collected by the workmen with a long iron rake, and formed into a bloom, which is afterwards carried to the tilt hammer, by which the slag is expressed, and its particles closely welded together in a compact When the loupe has by this means been welded into a form. solid mass, it is again put under the hammer, and cut by a kind of heavy steel knife into two equal portions, called massoques, which, after being a second time heated in the furnace, are made to assume the form of elongated prisms. Each of these is subsequently divided by a blow of the hammer on the back of the cutter into two equal parts or massouquettes, which are drawn out into bars during the first period of the succeeding operation.

Each charge requires six hours for its conversion into malleable iron, but during the last hour of fusion, those of the labourers who are not otherwise engaged are occupied in breaking the ores ready for the next operation, and sifting the greillade which is to be sprinkled on the surface of the fire.

The weight of the lump of metal thus obtained varies from 250 to 400 pounds, according to the size of the furnace, and the nature of the ores treated. In the Pyrenees, this quantity requires the expenditure of three times its weight of charcoal in its production, but in the Palatinate the amount of fuel consumed is frequently as much as seven times greater than that of the metal produced.

The metal obtained by this method consists of a variable mixture of iron and steel, the relative proportions of which are easily regulated by the way in which the furnace is worked; for if considerable inclination is given to the tuyere, and the siftings are plentifully thrown on the fire, the product is chiefly iron, whilst if the nozzle be nearly horizontal, and the greillade but sparingly supplied, a large product of steel is the result.

The Catalan method of iron making has been recently introduced into North America, and is extensively employed at Marquette and Carp River, on Lake Superior. In the arrangement there employed, the hearths, which are placed in long ranges on either side of quadrangular masses of brick-work, are supplied with hot air through water tuyeres of the ordinary construction employed in the English refinery. The bottoms of the hearths also consist of hollow cast iron plates, through which a current of cold water constantly passes. The working of these furnaces is conducted in every respect like that of the ordinary Catalan forge.

In Corsica, and along the whole of the Mediterranean shore of Italy, a furnace very similar to the Catalan is employed for the direct production of malleable iron. The hearth of this forge consists of a sort of semicircular basin, excavated on the top of a platform, in masonry, elevated about 3 feet from the surface of the workshop, in which it is placed. This raised mass of stone-work varies from 8 to 10 feet in length, and has a breadth of from 5 to 6 feet. The hearth itself, which is 18 inches in diameter, and 6 inches in depth, is formed in brasque, a mixture of charcoal dust and clay, and supplied with a current of air, by a nozzle slightly inclined, in connection with a water blowing machine or trompe. In this arrangement, although the operations of roasting, reduction and fusion, are carried on in the same furnace, they are nevertheless divided into two distinct processes, one of which consists in roasting and partially reducing the ores, and in the second the deoxidation of the half reduced ore is not only continued, but its fusion and agglutination also effected.

To arrange the furnace in order to accomplish the first stage of this process, a small quantity of charcoal in large pieces is arranged around the tuyere; this is again surrounded with a circle of broken and calcined ore from a previous operation, and enclosed in another circular wall of ironstone and charcoal; on the outside of this enclosure of charcoal, the ore to be roasted is piled in large lumps, and the whole afterwards covered with a thick layer of charcoal dust. The lumps of unroasted ore of which the outer circle is composed are so arranged that the larger and heavier masses are placed at the bottom of the heap, and firmly imbedded in the brasque of the hearth.

The smaller pieces are piled on this foundation, and slightly inclined towards the crucible, in order that being supported by the fuel within the enclosure, they may be more steady and less liable to fall. The fire is kindled by throwing some pieces of ignited charcoal into the inner circle, immediately before the tuyere; this is afterwards covered with large pieces of black charcoal, and the blast produced from a water blowing machine allowed to play into the hearth. At the expiration of about three hours, the processes of roasting and reduction are completed. The inner circle of roasted ore has now softened and run into lumps, whilst the outside wall of raw mineral is calcined, and ceases to give off either watery vapour or sulphurous fumes.

The fire is then extinguished, and after diminishing the outer wall of calcined ore, and removing the lumps of reduced metal, the furnace is prepared for the second operation. To do this, the hearth is entirely cleared out, and covered with a thick layer of brasque; two heaps of charcoal dust are also piled on either side of the furnace, and on the fuel, which is thrown into the cavity between them, are charged several pieces of the reduced metal obtained from the first operation. The blast is now admitted, and, by the reaction of the siliceous matters present on the unreduced oxide of iron, a very fusible slag is produced, which, together with the metal itself, soon becomes liquid, and falls through the ignited coal to the bottom of the hearth, where it accumulates. The carbon combined with the metal becomes oxidised by thus passing at a high temperature before the blast of the trompe, and the iron, which assumes a spongy form in the lower parts of the crucible, is at the close of the operation removed by an iron hook to be forged into bars under a heavy hammer. The slag, in proportion as it accumulates in the basin, is let off by the chio or floss-hole, whilst the furnace is constantly supplied with fresh pieces of partially reduced metal.

Each lump or bloom thus manufactured requires three and ahalf hours for its production, and weighs about 4 cwts. To make this, 10 cwts. of ore and 20 cwts. of charcoal are employed. Instead of burning all charcoal, a mixture of that fuel with dried wood is sometimes used, particularly for the first operation, in which the roasting and partial reduction of the ore is effected. The iron prepared in this way is of excellent quality, being soft and malleable; but the product is, in comparison to the quantity of ore and fuel employed, extremely small. The ore which in Corsica is thus treated is a specular oxide of iron, very similar to that s extensively worked in the island of Elba; but although it in reality contains 65 per cent. of metal, 40 per cent. only is obtained by the Corsican process.

In some parts of the Continent an apparatus is employed which holds a middle place between the low hearths of Catalonia and Corsica and the high blast furnaces now so generally adopted for the production of iron from its ores. These furnaces, called *stückofen* by the Germans, and by the French *fourneaux* à pièce, are, in fact, small cupolas, of which the height does not ordinarily exceed 15 feet, and of which the diameter at the hearth may be about 3 feet. This furnace is usually furnished with but one arch, by which the tuyere is introduced, and the extraction of the bloom effected. The blast is supplied by bellows moved by a waterwheel, and the slag escapes by a small floss-hole made at a certain distance above the bottom of the crucible. To extract the *stück* or bloom of spongy metal formed in the hearth, the bellows must be first removed, and a hole made in the masonry of the furnace, which is afterwards temporarily closed by a wall of bricks and potters' clay. This furnace, when filled up with charcoal, is lighted from the tuyere hole, and, when the mass has been properly ignited, the blast is admitted, and successive charges of roasted minerals and fresh charcoal supplied by the tunnel-hole. At the expiration of twenty-four hours, a considerable mass of agglutinated iron is found to have accumulated in the hearth, the side of which is now taken down and the mass removed by strong iron bars to a heavy hammer, where it is reduced into a cake of three or four inches in thickness, and subsequently divided into two equal parts. These pieces are afterwards refined in a small bloomery of peculiar form, where they are held, by powerful pincers, exposed to the action of a current of air from a nearly horizontal tuyere, by which means a portion of the metal flows down to the bottom of the hearth, where it accumulates in a spongy mass, and is drawn out into bars under a properly constructed hammer. In Carniola, where this process is employed in the treatment of a granular oxide of iron, the mass taken from the furnace at the expiration of each twenty-four hours amounts to from 18 to 20 cwts. This is afterwards subdivided into smaller pieces, which are first flattened under a heavy hammer, and then refined by being exposed to the action of a current of air which plays into a bloomery, the bottom of which is made of brasque. From the great quantities of charcoal required to produce a given amount of malleable iron, these methods are, however, falling

given amount of malleable iron, these methods are, however, falling rapidly into disuse, as it is found much more economical first to obtain the metal in the state of cast iron, and subsequently to oxidise the carbon which it contains by exposure to oxidising influences, than it is to prepare soft iron directly from the ore. The best iron manufactured is obtained from furnaces in which charcoal is the only fuel employed, since the impurities which always exist in every variety of mineral combustible in a greater or less degree combine with the metal and depreciate its quality.

For the manufacture of Steel, which will be now described, iron of the best quality only is employed. The iron most approved for this purpose is obtained from Sweden, and marked with the letter L in a circle; hence called the hoop L. The other varieties of Swedish iron, although superior to any made in this country, except the Ulverstone charcoal iron, is not so much esteemed as that from Dannemora thus marked; but very excellent iron of this kind is manufactured both in Russia and at Madras, and is largely imported into this country, where it is extensively converted into steel.

# MANUFACTURE OF STEEL.

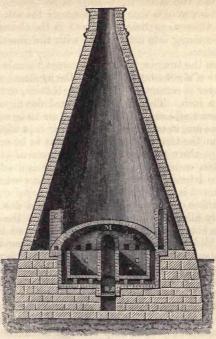
STEEL principally differs from wrought iron in containing a certain amount of combined carbon, and in being susceptible of having its hardness much increased by being first strongly heated and then suddenly cooled in water. Steel is also much more brittle than ordinary iron, but less so than crude or pig iron, which, besides containing a larger per-centage of carbon, is moreover, to a greater or less degree, combined with other impurities.

This substance is prepared for the purposes of the arts by two different processes, of which one is precisely the converse of the other, as steel may be made both by causing bars of pure malleable iron to absorb a proper amount of carbon, and also by effecting the partial oxidation of that which exists in large excess in some of the better kinds of cast iron. In this country the former method is exclusively adopted, and is known as "the process by cementation."

The furnace in which this operation is carried on is represented in the accompanying woodcut, fig. 144. It consists of an oblong rectangular building divided into two parts by a long and narrow fire-place, F, which passes through its centre, and is provided with a door at each extremity, by which the fuel is supplied. On each side of this is a chest or trough, c, made either of fire-tile or firestone grit, and so supported on bricks as to allow of the heat and flame of the fire passing beneath the troughs through the openings, in connection with the chimnies, o o. By these the smoke and heated air escape from beneath the dome, M, which is thrown over the two stone cases, and the fire-place by which they are heated. In the brick-work at one of the ends of these troughs openings are left for the purpose of introducing the wrought iron bars into the furnace; and by a larger aperture between the two troughs, which is bricked up during the working of the apparatus, the workmen are enabled to enter, when it has cooled, either to charge the bars of iron, or to remove the steel produced by their cementation.

The whole furnace is built under a conical hood, v, of from 30 to 40 feet in height, which serves both to prevent loss of heat by

radiation, and also to carry off the smoke and gases generated by the combustion of the fuel employed.



144.

The two chests vary from 8 to 15 feet in length, and from 2 feet 2 inches to 3 feet in width and depth; the smaller cases are found to produce steel of the most uniform quality, but are less economically worked than those of larger size.

The depth of the fire-place depends both on the nature of the fuel employed, and also on the dimensions of the cases to be heated: the space between these is usually about a foot in width, but in some instances one chest only is employed, and under these circumstances it is placed immediately over the grate on which the fuel is consumed. The degree of heat applied is regulated by opening or closing the openings in the dome, and limiting the amount of air passing into the furnace through the grate.

The cement is composed of hard charcoal very finely powdered,

to which is added about a tenth part of its weight of ashes, and a little common salt. The exact action exercised on the heated metal by the two latter ingredients is not clearly understood, although it is probable that the presence of the salt may tend to vitrify any siliceous particles contained in the charcoal, and prevent their entering into combination with the iron under process of carburisation.

To charge the troughs, the space between them is covered over with a plate of sheet iron, and on this the workman stands whilst he sifts a layer of cement evenly over the bottom, to the thickness of about an inch. This is firmly pressed down, and on it are regularly arranged the bars of iron which are to be converted into steel. These are, in order to allow for their expansion, cut rather shorter than the trough in which they are to be cemented, and are placed on their thinnest edge with a space of about half an inch between each bar. The same space is likewise allowed between the lateral bars and the sides of the case, and another layer of cement is now sifted in, and, after being equally spread over the surface of the metal, is firmly pressed down, so that it may entirely fill up the interstices left between the bars, which, if this were not scrupulously attended to, would, on being heated, become welded together in one mass. This second stratum of cement is about an inch in thickness, and on its surface is arranged another series of bars, in such a way that they may each rest on the cement filling the spaces left between the first layer in the bottom of the case. This is continued until the case is thus filled to within three inches of the top, when the remaining space is partially closed with old cement powdered, and afterwards covered over with a thick layer of damp siliceous sand. Sometimes, instead of using sand, the upper space is entirely filled with old cement, and in this case the top of the trough is closely covered over with refractory tiles, and the joints made tight by the application of fire-clay. Small openings are also left in the centre of the end stones of the cementing troughs: these are for the purpose of from time to time drawing out the extremity of a bar, in order to examine how nearly the process has advanced towards <sup>\*</sup> completion. The ends of these bars are left projecting a little beyond the cementing vessel, and as they correspond to small iron doors fixed in the outer brick-work, are easily seized and drawn out by a suitable pair of tongs.

When the furnace has been charged, and the iron platform removed, a little fire is thrown on the grate, and the heat gradually and carefully increased during the first twenty-four hours. If this were not attended to, the material of which the troughs are composed would be liable to split; and for this reason the fire is carefully conducted for a considerable time after it has been lighted. On the second day the full heat of the furnace, which should be about 100° of Wedgewood's pyrometer, is attained, and this is regularly kept up during the remainder of the time occupied by the process. If this be exceeded, the metal operated on will be liable to melt into one mass; and, if not kept to this temperature, a longer time will be required to effect the cementation. In proportion as the iron absorbs the carbon furnished by the cement of the troughs, the greater is its liability to melt; and, consequently, the metal will be more fusible towards the close of the operation than at its commencement.

When the cementation has attained the desired point, fuel is no longer supplied to the grate, and the furnace is allowed to cool during several days before commencing to remove the charge. On being taken out of the cases, the cemented bars are now found covered with numerous blisters, caused by the formation of gaseous products within the substance of the metal, and from this circumstance the substance so obtained is commonly known by the name of *blistered steel*.

The time required for the production of steel of moderate hardness, such as that called shear steel, may be reckoned, on an average, at from six to eight days. The softer kinds, such as those employed in the manufacture of saws and springs, require a proportionately shorter time for their preparation; but the very hard varieties, of which chisels and other cutting tools are composed, must be exposed to the carburising influence during two or three additional days. A furnace of this kind converts at one operation from eight to twelve tons of bar iron into blistered steel. The steel thus obtained is found to have absorbed about one-half per cent. of carbon; but, besides being subject to numerous fissures and cavities in its surface, its composition is far from uniform, and it consequently requires to be repeatedly faggoted and drawn out under a tilt hammer before it can be applied to the manufacture of cutlery and other objects requiring a dense and uniform material. The tilt hammer employed for this purpose weighs from 150 to 200 pounds, and is worked by a water-wheel, on the axle of which are placed cams, which, acting on the tail of the hammer, in rapid succession raise its head, and then allow it to fall heavily on the metal, which rests on an anvil placed immediately beneath it, and nearly on a level with the floor of the workshop in which the tilting is carried on. The workman who holds the mass under the hammer, and guides it so as to be drawn out into bars of the proper length and thickness, is seated in a cavity sunk for that purpose below the level of the floor, on a board which is suspended from the roof of the building by long iron rods. The hammer employed makes from 200 to 300 blows per minute, and the workman who is thus suspended is enabled by a slight impulse of his feet to move the bar in any position he may require with the greatest possible ease. Connected with each hammer is a forge hearth for heating the bars of steel: this is placed on a raised mass of masonry, and is supplied with a current of air by means of large bellows fixed just below the roof of the shop, and which communicate with the tuyere by a copper pipe. These bellows are set in motion by a small crank attached to the shaft of the water-wheel, and connected with the lower board by a stout wire acting on a simple lever.

The faggots of blistered steel are made by binding in a bundle, around a bar of double that length, four pieces of eighteen inches long, which are secured in their positions by a small band of wrought iron, which is subsequently removed. These faggots are placed in the forge hearth until they have attained a strong welding heat, when they are sprinkled with siliceous sand, in order to afford them a vitreous covering of fusible iron slag, and placed under the hammer, where they are first welded together, and afterwards drawn out into uniform rods of the size best adapted to the purposes for which they are intended to be used. The metal which has been thus treated is found to have become much denser and more homogeneous in its structure than before it was subjected. to the hammer, and is, consequently, not only capable of receiving a higher polish, but has also acquired during the operation a considerable amount of tenacity, malleability, and ductility, which much enhances its value for the manufacture of knives, springs, and many similar objects. The name of shear steel has been applied to this commodity, from the circumstance that the shears for dressing woollen cloths are commonly made from metal which has been thus faggoted, and afterwards drawn into bars. Each of the men employed at the tilt hammer is assisted by two boys, who take from him the bars which have been drawn out on the anvil, and in their place supply him with faggots heated to the welding point in the forge hearth. When the bars to be worked are small the heat acquired in the fire soon passes off, and the metal which, when first placed under the hammer, was red hot, quickly changes to a darker hue. By the rapid action of the hammer, the temperature is, however, in a short time again raised sufficiently to carry on the forging of the bar, and it is a curious sight to thus see a piece of metal forged by the heat developed by the intense friction and attrition set up between its own atoms. In the neighbourhood of Sheffield, where large quantities of this steel are prepared for the manufacture of cutlery, it is customary for the consumer to buy the blistered steel in its raw state, and afterwards send it to the tilt mill, where it is drawn into bars previous to being worked into knives, chisels, scissors, and other cutting instruments. The loss on the crude bars during this operation is estimated at from 5 to 8 per cent.

When, instead of causing pure iron to combine with a due proportion of carbon, steel is produced by the partial decarburisation of a superior kind of cast iron, the resulting product is known under the name of *natural steel*, which for many purposes is preferred to that obtained by the process of cementation as practised in this country. This variety is largely manufactured in many parts of Germany, and particularly in Styria and Silesia, where only the purest and best description of cast iron is employed in its preparation. The crude iron best adapted for this purpose is that obtained from spathose ores containing a certain portion of manganese, and which present, when broken, a shining lamellar fracture. This iron is produced in charcoal furnaces, and refined in a small bloomery, similar to that used in some parts of the Continent, for the production of wrought iron from the crude metal.

After having filled the hearth with burning charcoal, six or seven plates of lamellar cast iron are successively melted before the blast of the tuyere; these plates are from an inch to an inch and a-half in thickness, and are placed perpendicularly in the hearth. At the commencement of the operation, a certain quantity of rich slag and iron scale struck from the loupes by the large hammer is added to the charge, which, melting on the surface of the cast iron when in a fluid state, assists in the oxidation of the carbon which it contains.

When the first plate is in a perfectly liquified state, and has collected at the bottom of the crucible, it is at first nearly fluid, but being there subjected to the oxidising influences of the rich slags by which it is covered, it rapidly loses a portion of its combined carbon, and becomes thickened into a pasty mass. At this point another plate is fused by being brought directly before the blast, and this falling in drops to the bottom of the hearth, again gives fluidity to the whole mass of metal there accumulated. Under the united influence of the blast and the oxidising slags, this in its turn loses a portion of its carbon, and becomes pasty. A third plate is now melted in the same way as the two former ones, but care is taken that the falling drops of liquid metal may be received on the centre only of the molten mass which is collected at the bottom of the hearth. The middle of the loupe only is now melted by the fused cast iron, and this is surrounded by an annular ring of spongy metal which does not assume the liquid state. This operation is repeated until six or eight plates

of cast iron have been successively melted, at the expiration of which time from 300 lbs. to 450 lbs. of spongy iron will have accumulated at the bottom of the furnace. The scorize are at this point of the operation run off, and the loupe is raised from amongst the fuel by which it is covered, and divided into wedgeshaped fragments by being cut according to a series of lines radiating from its centre to the circumference. By operating in this way, the several masses of crude metal will be found to have a nearly similar composition, but as the cake from which they are cut is itself far from homogeneous, the different parts of the same fragment seldom exhibit precisely the same degree of carburisation. It consequently follows that these lopins, which are now drawn into bars, will yield rods very differently constituted at different points of their length. To remedy this defect, and to give at the same time greater density to the finished steel, the bars of rough metal are now handed over to the refiner, who, after having heated it red hot, and subsequently cooled it by plunging in cold water, raises each bar by one of its ends, and allows it to fall heavily on an anvil placed for that purpose on the floor of the workshop. By this treatment the most brittle part of the bar is immediately detached, and on striking a still harder blow in the same way, another and less carburetted fragment becomes broken off, whilst the larger portion which remains in the refiner's hands merely consists of a peculiar steely iron, which, in many countries, is much used for forming the teeth of harrows, plough-shares, and other agricultural implements.

The parts broken off by concussion are assorted according to the structure of the fractured ends, and are subjected to a series of manipulations destined to communicate to them greater density and uniformity of composition. For this purpose care is taken to weld together a piece of the hardest steel, and one which is much less carburetted; the bar thus obtained is afterwards heated, and hardened by being plunged into water, and this is again broken as before described, and subsequently united into one bar, and, if necessary, subjected to the same process until perfect uniformity of structure and composition has been obtained. It is easily perceived that by this treatment the desired result will be ultimately attained; but this is produced at a considerable expense of labour and fuel, and is attended with the loss of a greater or less portion of the crude steel employed. If this mode of treatment were carried too far, it is also evident that the whole of the combined carbon would be gradually removed, and the steel eventually reduced to the state of malleable iron. To prevent this, the surface of the faggoted bars is slightly covered with a coating of fine clay, which, uniting with a small portion of oxide of iron, gives rise to

the formation of a fusible slag, by which the enclosed metal is in a great measure protected from the oxidising influences of the blast. The steel made by this process is, when carefully prepared, of excellent quality, and is for many purposes preferred to that obtained by the cementation of malleable iron.

The preparation of steel is sometimes effected directly from the ores in the Catalan furnace before described, and by this process the whole of the steel employed in many localities is exclusively manufactured.

To prepare steel iron by the Catalan method, the founder greatly diminishes the quantity of siftings which are usually strewed on the fire during the process of smelting, and takes care to run off the clinker very frequently in order to diminish its decarburising influence on the metal: he also keeps the loupe, when formed, covered over with lighted charcoal, which prevents the blast from playing too strongly on the spongy and partially refined mass. It is, moreover, known by experience at what moment the operation should terminate, and the loupe is then cut into lopins, and drawn out into bars, which, after being hardened are broken on an anvil, and the harder portions carefully separated from the more steely iron, which, from its hardness, is for many purposes much esteemed.

Although the bars of steel may be made to acquire a tolerably uniform density and composition by repeated workings under the hammer in the way already described, yet this method of obtaining the result is both tedious and expensive, and it is, moreover, found impossible to produce steel having a perfectly homogeneous structure without subjecting it to fusion, at a very elevated temperature, in an arrangement properly constructed for that purpose. The steel which is to be fused, and thus converted into *cast steel*, is placed in a crucible made of refractory clay, which is afterwards strongly heated in an ordinary wind furnace in connection with a tall chimney, by which a strong natural draught is obtained. This furnace consists of a square prismatic cavity, of about one foot on each side, lined with good fire-bricks, and having a depth of about two feet from the surface of the platform to the fire-bars, by which the fuel is supported.

Immediately under the cover is a flue, about four inches by six, for conducting the smoke and gases into the chimney : this admits of being closed by an iron damper, by which the draught may be either regulated, or, if necessary, entirely shut off. In most instances several of these furnaces are arranged around the walls of the foundry at a height of a few inches only above the level of the floor, and are so constructed that the ash-pits, which are beneath the floor, are in communication with a gallery sunk below the laboratory, and covered over with an iron grating, which at the same time secures a firm footing for the workman and allows a free passage for the air necessary to the efficient and rapid combustion of the fuel. The crucibles, which for this purpose are made of a very refractory material, are placed in the furnace on a sole-piece of fire-clay, and are filled with pieces of blistered steel broken into small fragments, and sometimes protected from oxidation by the addition of a small quantity either of bottle-glass or furnace slag.

The charge of each crucible is about 30 lbs., and the fuel employed for its fusion is hard sonorous coke broken into pieces of the size of eggs. At the expiration of from three to four hours, the operation is completed, and the crucible being now withdrawn from the fire by tongs having strong concave jaws, the scorize on the surface are carefully removed, and the melted metal poured into rectangular, or eight-sided moulds of cast iron.

The steel thus obtained is much denser and harder under the hammer than that made by tilting the ordinary blistered bars into shear steel; it is also necessary to take considerable precautions in forging this material, as at a temperature a little above a cherryred heat it becomes so extremely brittle as to break when struck. Cast steel may, however, be welded by the interposition of a thin film of borax between the surfaces to be united, and it may be readily and firmly attached to iron by placing a bar of that metal having one well-polished surface in the mould into which the liquid metal is poured. By this treatment the steel becomes perfectly united to the polished surface of the iron bar, and is so firmly attached as to admit of both being rolled out together into rods of any given dimensions. The two metals, when thus united, are frequently employed for the manufacture of chisels, plane-irons, and other cutting instruments, in which the cutting edge being of steel, and the opposite side of iron, the hardness of the one and the toughness of the other are successfully combined.

A variety of cast steel known by the name of Wootz, or Indian steel, is prepared by the natives of that country by the treatment of a very pure ore consisting almost entirely of magnetic oxide of iron.

This ore, when extracted from the mine, is contaminated with a certain quantity of siliceous and earthy matters, from which it is separated by a process of winnowing principally carried on by women, who are extremely dexterous in this art. The furnace in which these ores are melted is entirely composed of refractory clay, and is from four to five feet in height. Its shape is that of a truncated cone, its internal diameter at the bottom being about two feet, whilst the upper extremity, or tunnel-hole, is not above one foot across. A furnace of this kind requires but a few hours for its erection, and is usually sufficiently dry on the following day to admit of being at once set in active operation. It is now filled with charcoal, which is ignited by the tuyere-hole near the bottom, and a current of air is supplied by a pair of sheep-skin bellows, of which the bamboo nozzles are united in a tube roughly made of fire-clay.

When the combustion going on within the furnace is considered sufficiently active, a portion of the ore, slightly moistened with water, is added on the top of the fuel, and another layer of charcoal again spread on its surface.

The operation is carried on in this way with successive charges of ore and charcoal during three or four consecutive hours; at the end of that time the blast is stopped, and, after opening the front of the furnace by destroying a portion of the clay wall, the bloom is removed by a pair of heavy iron tongs. The mass is subsequently beaten with heavy wooden mallets to express as much as possible of the slag, and after being cut into two parts to expose the nature of the metal, is sold to the native smiths, who make it into bar-iron.

To convert this iron into steel, the natives heat it in crucibles made of refractory clay mixed with a large quantity of rice-husk, and in these is placed, together with the metal to be converted, a certain portion of finely-chopped wood, for which purpose the *Cassia auriculata* is commonly preferred. The quantity of iron put into each crucible does not usually exceed a pound in weight, and, after covering the pots with one or two green leaves of the *Convolvulus laurifolius*, they are firmly closed with a little wetted clay, and placed in the sun to dry.

When the clay plugs have become sufficiently hardened, from 20 to 24 of these erucibles are built in an arched form on the bottom of a small blast-furnace, and strongly heated during from two to three hours with a blast produced as before described. At the expiration of this time, the conversion is considered to be completely effected; the furnace is then allowed to cool, and the crucibles are removed and severally broken, when the steel is found in the form of a rounded button occupying the bottom of each pot. The metal thus prepared is, for the purposes of the finer kinds of cutlery, preferred to the best specimens of English cast steel manufactured from selected Swedish bar-iron.

If a bar of steel be first strongly heated, and then allowed to cool very gradually, it becomes almost as soft as ordinary iron, and in this state admits of being filed, cut, or turned with the same facility. But if, after being thus made red hot, it be suddenly cooled by being plunged into water, or any other liquid, it becomes extremely hard and brittle, and is then said to be hardened. Steel thus treated is found to possess a lower specific gravity than before being hardened, but, on being again heated, and allowed to cool down gradually, its original softness and malleability are restored.

In manufacturing objects of steel, the metal is worked into the required form when in a soft state, and is subsequently hardened by being strongly heated, and suddenly cooled by immersion in cold water.

In doing this, however, it is found difficult to arrive at the exact degree of hardness best fitted for the purpose to which the instrument is to be applied, and it is therefore customary, in such cases, to give to the metal in the first instance a considerable degree of hardness, and afterwards render it more elastic and coherent by an operation called tempering, or annealing, in which the workman is entirely guided by the various colours assumed by the surface of the metal during the progress of the operation. These tints, some of which are extremely brilliant, are occasioned by very thin films of oxide corresponding with considerable exactitude to the degree of heat to which the metal is exposed, and consequently serve as a tolerably accurate guide in determining the state of hardness to which the object has been reduced.

The following colours will appear in succession on the surface of a plate of hardened and polished steel when exposed to a progressive heat. A piece of polished and hardened steel, subsequently heated to  $430^{\circ}$  Fahr., has a faint yellow colour, and is well suited for lancets and other instruments requiring an extremely fine edge. When tempered at  $450^{\circ}$ , a faint straw colour tint is obtained, which is well adapted for razors and surgeons' amputating knives. Steel seasoned at  $470^{\circ}$  is of a full yellow colour; this is tougher than the above, and is the tint to which pen-knives are usually tempered. At  $490^{\circ}$  it acquires a brownish-yellow tint, which is the colour best fitted for cold chisels and shears for cutting metals.

Axes and plane-irons are tempered at about  $510^{\circ}$  Fahr., which developes a brown shade intermixed with purple spots. For table-knives and cloth shears, a temperature of  $530^{\circ}$  is employed, which gives a purple colour to the metal so treated. For swords and watch-springs the metal is allowed to cool when of a bright blue colour: this tint very nearly corresponds with a temperature of  $550^{\circ}$  Fahr.

When heated to 560°, steel assumes a fine blue colour, and is

at this stage well adapted for small shears and ordinary chisels. At 600° it takes a dark blue colour, which is that best fitted for large saws, the teeth of which require to be bent by a hammer.

If, when the plate has assumed any one of these colours, it be allowed to cool, it will be found to still retain that tint, which will, at the same time, correspond to the degree of hardness imparted to the instrument thus tempered.

In order to reduce the hardness of steel which has been too highly carburised, or remove the excess of carbon united with the exterior portion of a bar of that metal, and consequently render its composition more nearly identical throughout its whole substance, it is merely necessary to expose it for a certain period to a cementing heat when imbedded in finely-powdered oxide of iron, or oxide of manganese. In this way the oxygen of the oxide gradually consumes the excess of carbon present, and if allowed to remain exposed to this action for a sufficient length of time, the steel first becomes externally converted into soft iron, and subsequently loses all its steely properties. A method of treatment analogous to this is sometimes employed for the decarburisation of ordinary cast iron, which, from the facility with which it may be cast into any desired form, possesses certain advantages over malleable or wrought iron, which can, by forging alone, be worked into shape. Stirrups, bits, buckles, and other objects, are, therefore, after being made of cast iron, occasionally transformed into malleable metal by a process of decarburisation analogous to that above described.

Steel, on being moistened with a drop of dilute nitric acid, yields a dark grey spot, whilst that obtained on malleable iron when so treated is of a green colour; and this test consequently affords a ready means of distinguishing between the two forms of this metal.

The cementation of steel may also be effected by exposing the metal at a proper temperature to the action of carburetted hydrogen gas, and on this principle a patent was some time since obtained; but although the steel thus produced is of excellent quality, the process nevertheless does not appear to be capable of economical application, and has consequently fallen into disuse.

The experiments of Stodart and Faraday have shown that when steel is fused with either platinum, silver, rhodium, or iridium, its hardness becomes much increased by the addition of but very small quantities of these metals; but such alloys have never been applied to the manufacture of ordinary cutlery, and are, consequently, rather matter of scientific interest than of commercial importance.

Keys and other objects, such as the locks of guns and various

small tools liable to become worn by friction, are sometimes externally converted into steel by a process of cementation which is arrested when the operation is supposed to be sufficiently advanced. Such articles are said to be *case-hardened*, and are still internally composed of malleable iron.

The damasking of steel, by which its surface is covered by a variety of figures resembling the water lines on some kinds of silks, is produced by repeatedly drawing out and subsequently doubling up and welding together a bar composed of a mixture of steel and iron. When an instrument, such as a bayonet or gun barrel, made of this metal, is washed with a weak acid solution, its surface becomes in a greater or less degree unequally attacked, and this gives rise to peculiar wavy figures, which may be observed on the once celebrated sword-blades of Damascus.

Analysis of Steel and Cast Iron.—Both steel and cast iron essentially consist of variable compounds of iron and carbon; but they also contain a certain amount of other substances, such as silicum, sulphur, phosphorus, and manganese, and I shall now briefly describe one of the more efficient methods by which these bodies may be successively separated from each other, and subsequently estimated.

The carbon contained in ordinary cast iron may either exist in the form of free disseminated carbon, or in a state of chemical combination with the iron itself. It is therefore necessary, in all analyses of these substances, to be enabled to distinguish between the amount of carbon so combined, and that which is only disseminated in a plumbaginous form. The quality of pig iron is also materially affected by the presence of even minute quantities of either sulphur or phosphorus, and it is consequently necessary to be enabled to detect and estimate these bodies with a considerable degree of accuracy. In this, as in most other analytical operations, it is first necessary to reduce the substance to be examined to the state of a very finely divided powder, in order that the various reagents, to the action of which it is to be subjected, may the more readily be enabled to produce the required modifications.

If grey pig iron of good quality is to be examined, it will be found to yield readily to the action of a new and well-tempered file, and the detached particles may be afterwards passed through a sieve of fine gauze, in order to separate the coarser fragments. When white cast iron is to be analysed, it will, from its extreme hardness, be found impossible to reduce it to powder by this means, as it not only almost entirely resists the action of the file, but the filings so obtained would to a considerable extent be contaminated by the particles rubbed off from the file itself. In this case the best method of reducing the metal to the required state of minute division, is to subject it to the repeated blows of a mallet or heavy hammer when placed in a cast-steel mortar of the kind employed for crushing some of the harder description of minerals, and afterwards passing the pounded metal through a gauze sieve to separate those particles which have not been sufficiently reduced in size. The powder obtained in this way may be analysed by several different methods, all of which are capable of yielding results of considerable accuracy; but none of these will be either more accurate or more readily performed than the following :—

The pulverised iron to be examined is divided into three distinct portions. In the first, is determined the total quantity of carbon present in the iron. In the second, the sulphur and phosphorus are estimated. And in the third, are determined the whole of its other constituents, with the exception of that portion of its carbon which exists in a chemically combined state.

Determination of Carbon.-For this purpose from 30 to 40 grains of the finely divided iron should be rubbed for a considerable time in an agate mortar, along with about its own weight of hard white sand, which has been previously mixed with a little oxide of copper, and ignited to destroy any adhering traces of organic matter. When an almost impalpable powder has been thus obtained (care being taken to prevent any loss by placing a sheet of highly glazed paper beneath the mortar), it is mixed with from six to eight times its weight of fused chromate of lead, and introduced with the usual precautions into a combustion tube, at the extreme point of which are placed a few grains of perfectly dry chlorate of potash. The combustion is now to be conducted in the ordinary way, and the carbonic acid produced, after passing through a chloride of calcium tube, is collected and weighed in a Liebig's apparatus, containing a solution of caustic potash of the specific gravity of 1.28. Nitrogen has hitherto never been found in any of the varieties of cast iron, but may be sought for, and if present, estimated by mixing the powdered metal with soda-lime, and recovering the products of combustion in a dilute solution of hydrochloric acid contained in a Will and Varrentrapp apparatus. The amount of chloride of ammonium found, if nitrogen be present, will be estimated in the usual way, and from it the percentage of nitrogen present is readily deduced.

Determination of Sulphur and Phosphorus.—The iron reduced to fragments is treated with fuming nitric acid, and gently warmed, when it becomes rapidly attacked, with the evolution of copious fumes of nitrous acid, which will not, however, contain any traces of sulphuretted hydrogen gas. The solution is now evaporated to dryness, and the dry mass subsequently treated with very dilute hydrochloric acid. To a little of the filtered solution a few drops of chloride of barium are added; and if, after standing for several hours, any precipitate or cloudiness appears, the whole of the filtrate is treated in the same manner, and the sulphate of baryta deposited, after being collected in a filter, washed, dried, and calcined, affords the data from which the per-centage amount of sulphur contained in the metal may be readily calculated. The excess of baryta is subsequently removed from the solution by the addition of a sufficient quantity of sulphuric acid, and tartrate of ammonia is then added to the amount necessary to prevent the precipitation of the iron by ammonia, which is at this stage of the operation to be added in considerable excess, and a current of sulphuretted hydrogen passed through the solution during several hours. The liquor is now allowed to remain in a warm place until it assumes a clear light-yellow colour, when it is quickly filtered, and the precipitate washed with distilled water containing a little sulphide of ammonium. The filtrate is at this point to be evaporated to dryness, the ammoniacal salt driven off by ignition, and the residue, consisting of phosphoric acid, together with minute portions of lime, alumina, and the alkalies, is fused in a platinum crucible with a small quantity of the mixed carbonates of potash and soda. The fused mass is then dissolved in hydrochloric acid, and the phosphoric acid determined in the usual way as ammoniophosphate of magnesia. Instead of operating in the manner above described for the estimation of the sulphur, this body may be detected, and its weight determined, by slowly dissolving the iron in weak hydrochloric acid, and allowing the hydrogen gas which is then evolved to pass through a somewhat acid solution of acetate of lead. Should any sulphur be present in the metal, it will by this treatment be converted into hydrosulphuric acid, which, combining with the metal of the lead solution, forms a sulphide from the weight of which the per-centage of sulphur present may be deduced. In this experiment the metal should be acted on with extreme slowness; from ten to fifteen days being required to dissolve the necessary quantity of cast iron, from eight to ten days for steel, and about four days for common wrought iron. This process, though much more tedious and not more accurate than that above given, may in some instances be advantageously employed for the purpose of checking the results obtained from the attack by nitric acid and the subsequent precipitation of the sulphur in the form of sulphate of baryta.

Estimation of the Uncombined Carbon, Metals, Silica, Lime, &c. —Another portion of the pulverised metal which should also weigh from 30 to 40 grains, is now placed in a small glass flask, and treated with dilute hydrochloric acid, which, on being gently warmed, will in the course of a few hours dissolve the iron, leaving black flakes and particles of a dark colour floating in the liquid. These are collected on a filter, dried at 212°, and of which the weight has been noted, and after well washing and subsequently drying the precipitate, the increase of weight will represent the amount of uncombined carbon, together with very minute traces of the silicates of the oxides of iron and lime. The silica, iron, &c., of this mixture are determined by fusing it with nitrate of potash, mixed with twice its weight of pure carbonate of soda; and on the separation of the iron, lime, and other earthy matters, the amount of carbon will correspond to the loss of weight experienced. To check these results, however, the flocculent residue may be collected by filtration through a piece of asbestos placed in the throat of a funnel, which, after being dried, may be acted on by chromate of lead or oxide of copper, according to the method usually employed for organic analysis. If the experiment be carefully conducted, the results obtained by these two methods will be found to agree very closely. The iron obtained in this way is added to the filtrate from the first solution, and the carbon found in the deposit (which may for the sake of distinction be designated b), on being deducted from the total quantity present, as found by the combustion above described, will give the quantity of combined carbon, which may be called a. The filtered liquid and washings are now evaporated to dryness, and again treated with dilute acid, by which a minute portion of silica is left undissolved; this, after being collected on a filter, is added to that already found in the black deposit, and the two are estimated together. A small quantity of the solution should at this stage of the analysis be treated with sulphuretted hydrogen gas; and if a dark-coloured precipitate be obtained, the whole of the filtrate should be acted on in the same way. When a dark deposit is thus obtained, it must be separated by filtration, and the metals which it contains determined by the ordinary course. If, however, as is generally the case, the small quantity of liquor thus treated gives no other than a milk-white precipitate of sulphur, it is, after being carefully freed from the precipitate by filtration, returned to the main solution. Nitric acid is now added to the filtrate, which is boiled until the whole of the iron is peroxidised; ammonia is added gradually until the solution only faintly reddens litmus, and the greater portion of the iron is thereby precipitated in the form of peroxide. The last traces of this metal are separated by the addition of a little neutral benzoate of ammonia, and from the weight of peroxide of iron found the amount of the metal originally present is deduced. After the weight of the oxide of iron has been obtained, a portion of it may be tested for minute traces of chromium and alumina, by dissolving it in hydrochloric acid, and precipitating with caustic pot-The quantities of these substances are commonly ash in excess. extremely minute; and if an excess of ammonia has not been added before treating with the benzoate of that alkali, the iron precipitate will not contain any traces of the oxide of manganese. Before proceeding to separate the manganese, the solution and washings are to be evaporated to dryness, and the salts of ammonia driven off by ignition to redness. After being thus treated the deposit has always a brown colour, from the presence of the peroxide of manganese, and it must now be dissolved in a few drops of hydrochloric acid, and after the addition of a little ammonia, and afterwards sulphide of ammonium, it is allowed to stand for several hours, and is then gently warmed. The sulphide of manganese thus deposited is collected in a filter, and may either be converted into sulphate of manganese, or dissolved in hydrochloric acid, and subsequently deposited in the form of carbonate, and weighed as the red oxide of that metal. The solution from which the manganese has been thus separated is now freed from sulphide of ammonium by boiling : the lime is precipitated in the form of oxalate by the addition of oxalate of ammonia. From the weight of carbonate of lime obtained from the ignition of this salt, the amount of lime is readily deduced, and from this is calculated the quantity of calcium originally present in the sample of metal analysed. If any magnesium were contained in the compound examined, its presence can now be detected by the addition of a few drops of a solution of phosphate of soda to the filtrate from the oxalate of lime; but this body has never yet been found in sufficient quantity for estimation, as traces only of this metal appear to enter into combination with the iron.

The presence or absence of magnesia in the compound having been established by qualitative analysis, it will in most instances be found to be so small in quantity as to be safely neglected in the quantitative determinations, and the solution from which the lime has been separated may at once be evaporated to dryness, and ignited to obtain the alkalies in the form of chlorides, in which state they are weighed. On dissolving these in a little water, and afterwards adding a few drops of bichloride of platinum to the solution, the potash is separated in the usual manner and weighed, and on deducting the weight of chloride of potassium from that of the mixed chlorides as obtained by direct experiment, the amount of chloride of sodium is readily deduced.

The following table indicates the per-centage composition of ten specimens of cast iron analysed by Mr. Wrightson, who employed in his investigations the methods above described. These specimens were made from the South Staffordshire iron ores, principally occurring in the districts lying to the west of the Dudley coal field.

# ANALYSES OF TEN SPECIMENS OF CAST IRON, MADE FROM SOUTH STAFFORDSHIRE IRON ORE, CHIEFLY WEST OF DUDLEY.

# IRON FROM COLD BLAST.

	I.	III.	IV.	ν.
Iron	94.10	96.57	94.53	94.42
Combined Carbon (a)	1.87	0.95) C	С	
Uncombined Carbon (b) .	. 1.92	1.67 1.98	3.71 1 2.73	4.05
Silica	1.30	0.51) 1.30	9.11 - 4.19	
Manganese	1.12	1.16	0.33	0.94
Cobalt	trace			trace
Chromium	trace	and the second second	n- notally	100
Calcium	0.05	trace	0.25	0.16
Sodium	0.16	trace	0.30	0.34
Potassium	trace	0.42		
Sulphur	trace	0.11	0.05	trace
Phosphorus	0.21	0.36	0.03	0.36
			The states	
	100.73	101.75	99.20	100.27

## IRON FROM HOT BLAST.

	I.	II.	III.	IV.	v.	VI.
Iron	89.53	92.98	93.84	92.90	95.23	95.80
Carbon )	С	C	С	С	(C(a)1.77	2.72
Carbon >	3.27 7.93	3.11 6.51	2.98 5.54	0.87 6.83 -	C(b) 0.49	0.26
Silica, &c.)	Same and				0.31	0.11
Manganese	1.71	1.30	0.72	0.62	0.34*	0.54
Calcium	0.11	trace	0.34	0.06	0.10	0.06
Sodium	0.41	0.37	0.39	0.30	0.19	0.14
Potassium	-	HEAL -	trace	trace		
Sulphur	0.02	trace	minute trace	e trace	trace	trace
Phosphorus	0.54	lost	0.07	0.40	0.12	0.37
	100.30	101.19	100.90	101.11	98.55	100.00

A very small amount of phosphorus is found to impart to iron a great degree of brittleness; when bar iron contains but 0.5 per cent. of this substance, it becomes *cold short*; but when a smaller quantity is present, it has only the effect of hardening the metal,

<sup>1</sup> The figures 3.71 in No. IV (cold blast), as well as in the corresponding figures in No. V. (also cold blast), and Nos. I. II. III. IV. (hot blast), indicate the per-centage of substances separated and weighed on the filter, consisting, with the exception of No. IV. (hot blast), principally of silica, with the oxides of iron and lime, which were not in these instances separately estimated. The figures marked C, on the left of the columns, indicate the entire amount of carbon, both combined and uncombined, contained in the iron examined.

without materially influencing its other properties. The presence of sulphur in wrought iron causes it to break with great facility when heated; and when bar iron contains no more than 0.0001 of this body, it becomes extremely difficult to work at a welding Wrought iron of ordinary quality may contain about 0.25 heat. per cent. of carbon without being rendered steely and capable of being hardened by sudden cooling in water; but when it is contaminated with from 0.50 to 0.60 per cent. of its weight of this substance, it exhibits many of the peculiar properties of steel, and emits sparks on being smartly struck with a flint. The quantity of carbon necessary to render iron steely, is, however, in a great measure dependent on the purity of the metal itself, as, when it contains a small proportion of sulphur or phosphorus, it is rendered much more brittle and hard by a given amount of carbon, than when the same proportion is combined with a purer description of metal. Shear steel, of which the texture and composition have been equalised by repeated tiltings, contains from 1 to 1.5 per cent. of carbon. When steel contains a more considerable amount of this substance it becomes harder, less tenacious, and more difficult to weld; and when the quantity of carbon present exceeds 1.75 in 100 parts, the compound no longer admits of being welded at any temperature. Iron containing 2 per cent. of carbon does not admit of being forged under the hammer, and this may be regarded as the test by means of which cast iron is distinguished from highly carburetted steel. Iron containing 1.9 per cent. of carbon still admits, if carefully treated, of being worked under the hammer; and we may therefore regard this as the extreme point of carburisation, beyond which steel is converted into cast iron. When cast steel contains 1.9 per cent. of carbon, it is no longer applicable to the purposes to which less highly carburetted metal is applied, but still does not deposit any graphitous scales by fusion and slow cooling. When, however, the metal is combined with from 2.5 to 3.0 per cent. of carbon, a portion of that substance is readily eliminated by the slow cooling of the fused mass.

The properties of cast iron are not entirely dependent on the total amount of carbon which it contains, but are also to a great extent influenced by the state of combination in which the two substances exist.

Grey cast iron contains only from 2 to 2.5 per cent. of carbon in a state of chemical combination, the remainder being merely disseminated through the mass in the form of minute graphitous scales. Iron of this description requires for its fusion a much higher temperature than the white variety, in which a great portion of the carbon is chemically combined, and passes almost suddenly from the solid to the fluid state, whilst white cast iron becomes pasty before it is reduced to the fluid form.

Grey cast iron may be transformed into white metal by sudden cooling, and white iron admits of being converted into the grey variety by being first strongly heated, and then allowed to cool very gradually.

The principal localities in Great Britain where the manufacture of iron is extensively carried on, are Shropshire, South Staffordshire, Derbyshire, and the West Riding of Yorkshire, in England; Glamorganshire, in South Wales; and the district lying east of Glasgow, in Scotland.

The total number of blast furnaces at this time at work in the United Kingdom exceeds 600. Most of the new furnaces recently erected have been constructed with larger hearths and wider tunnel-holes than were formerly employed.

By far the largest proportion of the steel manufactured is prepared in the neighbourhood of Sheffield, where Swedish iron, principally from the Dannemora mines, is extensively employed.

The annual quantity of steel produced in Sheffield during the last five years varies from 17,000 to 18,000 tons from foreign iron, and from 1,500 to 2,000 tons from iron of British manufacture.

The number of furnaces employed in the neighbourhood of Sheffield for the conversion of iron into steel, is upwards of 120: each of these is capable of converting, weekly, six tons of iron, and consumes during the process a quantity of coal about equal to the weight of the steel produced. There are also above 100 steel melting furnaces, each on an average containing 10 holes for crucibles; four tons of good hard coke are required to make one ton of cast steel; and each furnace of ten holes produces  $4\frac{1}{2}$  tons of melted steel per week.

The total quantity of coals annually consumed in the town and neighbourhood of Sheffield, in the various processes relating to the manufacture of steel alone has been calculated at 250,000 tons.

## COPPER.

## Equiv. = 31.66. Density = 8.80.

THIS metal appears to have been known in the remotest antiquity, and, alloyed with about one-tenth part of its weight of tin, was employed, previous to the discovery of iron, for making all kinds of edge-tools and instruments of war. Copper, with the exception of titanium, is the only metal which has a strong red colour; it is very malleable, ductile, and tenacious, and, when warmed or rubbed, exhales a peculiarly disagreeable and characteristic odour.

The copper met with in commerce is seldom chemically pure, but is contaminated with other metals, such as lead, iron, and antimony; it also almost invariably contains traces of carbon and suboxide of copper.

Chemically pure copper may be obtained by reducing to the metallic state the pure oxide, by passing over it a stream of hydrogen gas, while heated in a hard glass tube. Under these circumstances the reduction takes place below a red heat, and the metal which remains in the tube is found in the state of a red powder, readily assuming a metallic lustre when rubbed between two hard surfaces.

The specific gravity of this metal varies slightly, in accordance with the nature of the treatment to which it has been subjected; as hammered or rolled specimens have a greater density than ordinary fused copper, which has not been thus compressed. The density of copper varies between 8.78 and 8.96; it melts readily at a strong red heat, and, when heated to whiteness, gives off very distinct vapours, which have the property of imparting a green colour to flame.

When copper is at ordinary temperatures exposed to the action of perfectly dry air, its surface is not in the slightest degree oxidised; but if acted on by a damp atmosphere, and particularly when acid vapours are present, it quickly becomes covered with a green substance, known by the name of verdigris.

If a piece of this metal, slightly moistened by a weak acid, be

left for a considerable time exposed to the contact of air, it at first combines with a portion of its oxygen, and forms a neutral salt of copper, which is subsequently converted, by the further action of oxygen on another atom of metallic copper, into a less soluble subsalt, which adheres firmly to the surface of the mass.

A fragment of copper wetted by ammonia, and exposed to the air, is oxidised in a similar way, and sheet copper is found to be rapidly attacked by weak solutions of chloride of sodium, although, when in a concentrated form, this salt acts but feebly on the metal.

Water is decomposed by copper when heated to whiteness in an atmosphere of steam: oxide of copper is formed, and hydrogen gas eliminated. A concentrated solution of hydrochloric acid attacks it, when in a state of fine division, with considerable facility; but when the copper is exposed to its action in more solid masses, its solution is attended with much difficulty.

The presence of the stronger acids does not determine the decomposition of water by this body. When dissolved in concentrated sulphuric acid, sulphurous acid gas is plentifully evolved.

Nitric acid, even when cold and considerably diluted with water, dissolves copper with great facility, and gives rise to the rapid evolution of binoxide of nitrogen, which, coming in contact with the oxygen of the air, produces large quantities of the characteristic red fumes caused by the resulting compound.

The tenacity of copper is less than that of iron, but greater than that of either gold, silver, or platinum.

Native Copper.—This metal frequently occurs in a native or malleable state, and is in all probability the result of certain electro-chemical influences, by which the sulphate of copper arising from the oxidation of its various sulphides is made slowly to deposit the metal which it contains on various points of the lode in which the different ores of copper are found.

Native copper is most frequently met with in irregularly-shaped masses, occupying the fissures of the rocks in which it is situated; but it is sometimes also observed in a crystalline state, and in this case the crystals are either cubes, octahedrons, or some of their immediately derived forms.

Native copper is both malleable and ductile; has a red colour, metallic lustre, and shining streak; possesses no traces of cleavage; and readily fuses before the blowpipe into a well-defined metallic globule, which, on cooling, frequently becomes externally coated with a thin layer of black oxide.

In some localities specimens of this metal occur in a perfectly

pure state, but it more frequently contains traces of other metals, and particularly iron and silver.

This substance is abundantly met with in the copper mines of Cornwall, Brazil, and Siberia, as also in the district to the south of Lake Superior, where masses exceeding one hundred and fifty tons in weight have sometimes been extracted. Most splendid crystalline specimens are also procured from Siberia and the island of Nalsoe, in Faroe, where it accompanies fibrous mesotype in amygdaloidal trap.

These crystals of copper are, generally speaking, far from regular, and present some of their dimensions in a much more developed state than others: the crystalline forms are usually most perfectly represented at the extremities of the branches produced by the union in rows of the more compressed and less perfectly formed examples.

#### ORES OF COPPER.

The minerals of which copper forms an essential constituent are extremely numerous and important, but we shall in the present instance chiefly confine our attention to such as are metallurgically treated for the metal they contain, and which are consequently entitled to be ranked among the ores of copper.

**Dinoxide of Copper**; Octahedral Copper Ore; Cuivre oxydulé; Kupferroth.—This oxide is remarkable for its fine cochineal-red colour, which may be observed with great readiness, particularly in transparent and translucid specimens.

This oxide crystallises in the cubic system, and most frequently occurs in well-defined crystals of a ruby-red colour. Its lustre is semi-metallic, streak shining and reddish-brown, fracture hackly or sometimes conchoidal, and its cleavage, which is much interrupted, parallel to the faces of the octahedron. When the crystals of this mineral are opaque, they are sometimes of an iron-grey tint on the surface, but their peculiar red colour at once becomes apparent when they are reduced to the state of a finely-divided powder. This oxide has a density of 5.99, and its composition, according to an analysis of Chenevix, is as follows :—

Copper			88.78
Oxygen			11.50

These numbers correspond to two atoms of copper united to one equivalent of oxygen, and its formula will consequently be represented by  $Cu_2O$ .

Octahedral oxide of copper is found in many of the Cornish mines, and particularly at Huel Garland, near Redruth.

Isolated crystals, sometimes an inch in diameter, are also obtained at Chessy, in the neighbourhood of Lyons; and many splendid specimens have been brought from Moldawa, in the Bannat, and Ekatharineburg, in Siberia. This suboxide is sometimes also found in extremely slender reticulated crystals: specimens of this variety are occasionally obtained from the mines of West Cornwall and Rheinbreitbach, on the Rhine.

**Black Oxide of Copper;** Cuivre oxydé noir; Kupferschwartz. —In a great many copper mines a black substance is found, which stains the fingers when handled, and is principally composed of oxide of copper mixed with various earthy impurities. Analysis shows that this substance sometimes contains sulphur and arsenic, and often considerable quantities of the oxides of iron and manganese.

From this circumstance it would appear that the black oxide of copper, which in many localities is obtained in sufficient abundance to render its extraction an important consideration, is the result of the decomposition of some of the other ores, such as copper pyrites, and that the traces of sulphur and arsenic which it still retains, are merely the result of an incomplete decomposition of such minerals.

This substance is commonly found disseminated among other ores of copper, and sometimes occurs in shining botryoidal concretions or dull friable masses.

Sulphide of Copper; Vitreous Copper; Cuivre sulfuré; Kupferglas.—Sulphide of copper is of an iron-grey colour, and is often iridescent; it is sometimes found in crystals, but more frequently in compact lamellar masses, and pseudomorphous crystals have occasionally been discovered, especially at Frankenberg, in Hessia. The primitive form of crystallised sulphide of copper is a sixsided prism, but the specimens obtained from the Cornish mines, and especially from Cook's Kitchen, in the neighbourhood of Redruth, frequently present themselves in thin hexahedral tables. This ore is extremely friable, and when scratched affords a shining streak.

When quite pure it may be readily cut with a knife, and is fusible in the flame of an ordinary candle. Its density varies, according to the texture of the specimens, from 5.5 to 5.8, and the crystals possess a distinct cleavage, parallel to the faces of the original prism.

Sulphide of copper is almost always contaminated with a certain portion of sulphide of iron, which considerably interferes

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with its hardness and fusibility; but the specimens obtained from Siegen are comparatively free from this impurity.

The composition of a specimen of this ore, from Cornwall, analysed by Thompson, was found to be as follows :----

Sulphur Copper	:	•	:	·	•	$20.62 \\ 77.16$
Iron	•	•	·	·	•	1.15
						98.93

These numbers indicate that this ore is a compound of two atoms of copper united to one equivalent of sulphur, and its constitution will therefore be expressed by the formula Cu<sub>2</sub>S.

Although magnificent crystals of sulphide of copper are sometimes obtained from the Cornish mines, they are nevertheless almost exclusively confined to that county; but the more compact and massive varieties also occur in Siberia, Hessia, Saxony, the Bannat, and, according to Silliman, in Nova Scotia.

**Copper Pyrites**; Cuivre pyriteux; Kupferkies.—This mineral is distinguished by its strong metallic lustre and deep brassyellow colour. It usually occurs in amorphous masses, with an irregular and slightly conchoidal fracture: it is also found in mammillated, stalactitic, and botryoidal forms, as well as in tetrahedral and octahedral crystals. Its specific gravity varies from 4.1 to 4.3, and, when strongly heated on charcoal before the blowpipe, it readily fuses into a dull-black globule, which, from the presence of iron, speedily becomes magnetic. When mixed with a little carbonate of soda, and similarly treated, it yields a button of metallic copper: if dissolved in nitric acid or aqua regia, it affords a solution, which, on the addition of ammonia, assumes a fine blue colour.

Copper pyrites is a double sulphide of iron and copper, consisting of one equivalent of protosulphide of iron united to one atom of sulphide of copper, and its composition will consequently be expressed by the formula CuS + FeS.

The following numbers show the composition of specimens of this substance from two different localities :---

	A	From Cornwall nalysed by R. Ph	From Ramberg. lysed by H. Rose.
Sulphur		. 35.16	 35.87
Copper .		. 30.00	 34.40
Iron .	•	. 32.20	 30.47
Gangue		. 2.64	 0.27
		100.00	101.01

This mineral is found in lodes or veins, which usually occur either in granite, grauwacke, or clay-slate, although it is sometimes met with in serpentine, gneiss, and some other rocks. It is most commonly associated in these deposits with iron pyrites, blende, and galena, together with the carbonates and other ores of copper commonly produced in Europe.

The principal localities in which this valuable ore is found, are Cornwall and Devon in England; Chessy and Saintbel, near Lyons, in France; in Saxony; at Eisleben and Stangerhausen, in Prussia; at Goslar, in the lower Hartz; at Kremnitz and Schemnitz, in Hungary; at Fahlun, in Sweden; at the Ural mountains, in Russia; as also in China, Japan, and at the Burra Burra mines in South Australia.

The Cornish copper ores, so extensively treated in the neighbourhood of Swansea, are almost entirely composed of this mineral, and constitute about five-sixths of the whole amount of copper raised in the United Kingdom.

The total annual produce of copper in Great Britain is estimated at about 18,000 tons, besides which, large quantities are annually imported from Cuba, Chili, and Australia, to be smelted in the various metallurgical establishments of South Wales.

This ore, although of extremely common occurrence, is not, however, usually brought into the market in a very pure state, as, from the great cheapness of fuel in the neighbourhood of the furnaces, and the facilities afforded by a short water-carriage, it is found more economical to directly treat the poorer ores, than to concentrate them beyond a certain point by means of a more extended mechanical preparation.

The ores sold at Redruth, in Cornwall, where the mineral products of the Western division of that county are principally disposed of, rarely yield above 12 per cent. of metallic copper, and even 8 per cent. of metal may be considered about a fair average of the produce of the total quantity of ore sold.

**Phillipsite**; Cuivre panaché; Buntkupfererz.—This ore, which, particularly since the reworking of the mines in Tuscany, holds a somewhat important position among the minerals producing copper, was for a long time confounded with copper glance, although in many particulars they are different.

This ore has a reddish-brown colour, and almost metallic lustre; its surface is commonly iridescent with different shades of blue, purple, and red, from which circumstance it is sometimes called *cuivre panaché*, by French mineralogists.

Fused before the blowpipe, it presents similar reactions to those obtained from ordinary copper pyrites, but when found in a crystalline form, the crystals are either cubes or octahedrons, of

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which the surfaces are not usually well-defined. It occurs in the compact form, associated with the green carbonate of copper, in Cornwall, Siberia, Hessia, Silesia, Norway, and the Bannat; also at Killarney, in Ireland, and in the cupriferous shale in the neighbourhood of Mansfeld.

The crystallised varieties of this mineral have as yet only been found in Cornwall, where it occurs in the Dolcoath and Tincroft mines, in the neighbourhood of Redruth.

This, like ordinary copper pyrites, is, although not combined in the same proportion, a double sulphide of copper and iron. Its atomic constitution is represented by the formula  $2Cu_2S + FeS$ , and its per-centage constitution, according to the analysis of Phillips and Varrentrapp, is as follows:—

		Fr	om Cornwall,	Fr	om Killarney,
		٦	Varrentrapp.		Phillips.
Copper			58.20 -		61.07
Sulphur			26.98 -		23.75
Iron .			14.84 -		14.00
Gangue		•	" -		0.20
			100.02		99.32

The specific gravity of the crystallised variety varies from 4.9 to 5.1, and the different faces of the crystals are, in many specimens, slightly curved.

Grey Copper Ore; Cuivre gris; Fahlerz.—Usually occurs massive, but sometimes also crystallised, in well-defined cubes and tetrahedrons. Its colour varies from steel-grey to iron-black, and when scratched yields either an unchanged or slightly brown streak. It has a conchoidal fracture, and sometimes an imperfectly developed cleavage parallel to the faces of the octahedron. It is exceedingly brittle, and has a density varying from 4.6 to 5.1.

Rose, who has made a very important series of investigations on the constitution of this mineral, has arrived at the conclusion that its general composition may be represented by the formula  $Fe_4Cu_{18}Sb_6S_{21}$ , but in which each of the different metallic constituents may be, to a greater or less extent, replaced by the substitution of other isomorphous elements; so that sulphide of antimony may be substituted for the sulphide of arsenic, and sulphide of silver for sulphide of copper, &c. &c.

This mineral also frequently contains zinc and silver, and occasionally gold and platinum. The following analyses of different specimens of this ore will serve to illustrate its variable constitution :---

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#### BLUE CARBONATE OF COPPER.

Locality.	Sul- phur	Anti- mony.	Arse- nic.	Copper.	Iron.	Zinc.	Silver.
Grey Copper, from Claus-	ber the			mal	- me	A.S.V.S	String (
thal, Rose	24.73	28.34	66	34.48	2.27	5.55	4.97
Do. from Wolfach, Rose	23.52	26.63	66	25.33	3.72	3.10	17.71
Ditto, from Corbiers,	a dvis			1.6.5.0	6.3	1 Carlos	1910 3
Berthier	25.30	25.00	1.50	34.30	1.70	6.30	0.70
Do. from Gersdorf, Rose,	26.33	16.52	7.21	38.63	4.89	2.76	2.37
Locality not named,	22.64	100		11/3-2	5-18 P.P.	1 NES	12.20
Klaproth	10.00	66	14.00	48.00	25.50	66	0.50
	18.50	23.00	0.75	40.25	13.50	66	0.30

Some of the finest crystals of this substance have been obtained from the mines near St. Austell, in Cornwall, and very beautiful complex crystals, of a bright polished aspect, are found at Andreasberg, in the Hartz; Kremnitz, in Hungary; Freyberg, in Saxony; Dillenburg, in Nassau; and Kapnick, in Transylvania: besides occurring in the above localities, the massive variety is found at Schwatz in the Tyrol, and in Siberia. This mineral is not only important as an ore of copper, but is frequently much increased in value on account of the silver, which, in greater or less quantity, it almost invariably contains.

Blue Carbonate of Copper; Azurite; Kupferlazur.—This mineral, which occurs both in mammillated concretions, and in welldefined and very brilliant crystals belonging to the rhomboidal system, of which the lateral faces form an angle of 98° 42′, is of a beautiful blue colour, and is sometimes perfectly transparent, although more commonly only translucid. Its specific gravity varies from 3.7 to 3.9, lustre vitreous or adamantine, fracture conchoidal, and streak of a somewhat deeper blue than that of the mineral itself. When acted on alone before the blowpipe, it is melted by the oxidising flame into a black globule. By the reducing flame a bead of metallic copper is obtained. It dissolves with effervescence in nitric acid, and yields a solution, affording all the common reactions of copper. When fused with borax in the oxidating flame, a glass of a bright green colour is produced.

Its composition, according to the analyses of Karsten and Phillips, is as follows :---

au barraniurbara verere	Specimen from Chessy,		Specimen from the Bannat,
	by Phillips.		by Karsten.
Oxide of copper	. 69.08		69.08
Carbonic acid	. 25.46	-	25.72
Water	. 5.46		5.20
	It is a second second		Li y the state
	100.00		100.00

#### COPPER.

The above numbers correspond to the formula 2  $(CuO, CO_2) + CO_2, HO$ .

This mineral occurs associated with the red oxide and the green carbonate of copper, and is found both in the primitive and secondary formations. The chief localities from which blue carbonate of copper is obtained, are Chessy near Lyons, Siberia, and the Bannat. Examples of this ore are also found at Redruth, in Cornwall; Alston-Moor, in Cumberland; in the Cuban mines, and at Burra Burra, in South Australia. When obtained in sufficient quantity, this substance constitutes a valuable ore of copper; it is likewise, when ground to a fine powder, occasionally used as a blue pigment, but from having a tendency to lose its original hue, and become green by exposure to light and air, it is at present but little employed for this purpose.

**Malachite**; *Cuivre carbonaté vert*; *Malachit.*—Green carbonate of copper is remarkable for its fine emerald-green colour, of which the same specimen usually exhibits a great diversity of shades. When in a crystalline state, this substance is found in forms derived from the oblique prism, of which the lateral faces form an angle of 107° 16′, but it is more frequently met with in mammillated reniform masses, and compact amorphous fragments.

Malachite, although rarely found in the crystalline form above described, frequently presents itself in the shape of variously modified octahedrons, produced by the conversion into carbonate of the dinoxide, or ruby-red ore, as also in oblique prisms of a fibrous internal structure, derived from the decomposition of the blue carbonate. It is likewise found in stalactiform masses, having a fibrous radiated structure made up of several successive layers, of which the extent and thickness are readily apparent and well defined. It is sometimes met with in a friable and pulverulent form, and is in that case commonly associated with various sandy and earthy impurities.

Malachite is found in considerable quantities in the Ural mountains; in the mines of Southern Australia; in the Island of Elba; at Chessy, in France: in the old mine at Sandlodge, in Shetland; in the Bannat, the Tyrol, and in some of the Cornish mines. It is, from its high per-centage of metal, and the facility with which it admits of being smelted, a valuable ore of copper; but is also highly prized by the lapidary for various ornamental purposes. Such varieties as are sufficiently compact are often cut into snuffboxes, and mounted as brooches, studs, and other articles of jewellery; and in Russia, polished plates of this substance are made up into tables, sideboards, and other objects of luxury.

The density of this ore varies from 3.6 to 4.0; lustre adamantine, inclining to vitreous; streak of a rather paler green than the mineral itself.

#### OTHER MINERALS CONTAINING COPPER.

Oxide of copper Carbonic acid . Water	 • •	b	From Siberia, y Vauquelin. 70·10 21·25 8·45	Also from Siberia, by Klaproth. — 71.70 — 20.50 — 7.80
			99.80	100.00

Its per-centage composition is as follows :---

The above numbers indicate that this substance is a dihydrated carbonate of copper, of which the composition is represented by the formula 2 (CuO, CO<sub>2</sub>) + HO. Carbonate of copper is advantageously employed to mix with the various sulphides of copper, during the operation of smelting, and for which it serves as an economical and effective flux. It is also employed as a green pigment, for the use of artists, affords a valuable material for the manufacture of the various salts of copper, and is particularly adapted for being converted into Roman vitriol, by solution in dilute sulphuric acid, and subsequent crystallisation.

Other Minerals containing Copper.—The other minerals, of the composition of which copper forms an essential ingredient, are extremely numerous and interesting; but as these seldom occur in sufficient quantities to constitute, properly speaking, ores of this metal, they present greater interest to the mineralogist than to the smelter.

Selenide of Copper is a rare mineral, isomorphous in composition with the sulphide; it is of a tin or silver-grey colour, is fusible like the sulphide, and is readily cut with a knife. The arsenides of copper are numerous, but of little importance in a commercial point of view. Euchroite, which is found at Libethen, in Hungary, is an emerald-green mineral, containing 33 per cent. of arsenic acid, and 48.0 of oxide of copper. Aphanesite is of a darker green colour, inclining to blue, and contains 30 per cent. of arsenic acid, and 54 of oxide of copper. This variety comes from Cornwall. Erinite, from Limerick, in Ireland, occurs in mammillated coatings, is of an emerald-green tint, and contains 38.8 per cent. of arsenic acid, and 59.4 of oxide of copper. Copper mica, found in Cornwall, and Hungary, is of a grass-green colour, and occurs in remarkably thin laminæ: it contains 21 per cent. of arsenic acid, and 56.4 of oxide of copper. Condurrite is an arseniosulphide of copper of a greenish black or blue colour, and is chiefly found in the mines of Cornwall.

Of the phosphates of copper there are three distinct varieties— *Pseudo - Malachite, Libethenite,* and *Thrombolite.* The first is found in some parts of Hungary, and at Bonn on the Rhine; it

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is of a dark or emerald-green colour, and occurs either in very oblique crystals, or as a massive incrustation on the surface of other minerals. The second, specimens of which are found in Hungary and Cornwall, is a dark or olive-green substance, occurring either massive or in slender prismatic crystals, containing 64 per cent. of oxide of copper. The third and last variety is a green phosphate, occurring in Hungary, and containing only 39 per cent. of oxide of copper.

Sulphate of Copper is found in a crystallised state in many of the mines from which copper pyrites, and the other sulphides of copper, are obtained. This salt, when produced by natural causes, resembles in every respect that obtained by artificial means; it crystallises according to the sixth crystalline system, has a fine blue colour, and is formed by the decomposition of the other ores of copper.

Atacamite.—Chloride of copper is a mineral of a green, or greenish black colour, and adamantine or vitreous lustre. It occurs in massive fragments, in rhombic prisms and rectangular octahedrons, which give off fumes of hydrochloric acid gas when heated before the blowpipe. This compound is found in Saxony, the neighbourhood of Vesuvius, and the desert of Atacama, between Chili and Peru. In Chili this mineral is ground into powder, and sold under the name of *arsenillo*, as a sand for dusting letters.

The other minerals containing copper are rare, and are, consequently, not treated as a source of the metal they contain.

# ESTIMATION OF COPPER, AND ITS SEPARATION FROM OTHER METALS.

This metal is estimated either in the state of metallic copper, or of black oxide. When it is to be weighed as metallic copper, it may be precipitated from its solutions by the introduction of a bar of either iron or zinc: in this case it should be rapidly washed with distilled water, and subsequently dried in such a way as to protect it as much as possible from the action of the air, by which it is rapidly oxidised. It will, however, in most instances be found advantageous to convert the granular copper into the black oxide, by a continued roasting in a small porcelain crucible, over the flame of a gas jet, or spirit lamp; as it is, even with the most skilful manipulation, extremely difficult to prevent the absorption of a small quantity of oxygen by the finely powdered metal, and this, by increasing the weight of the product, vitiates the results obtained. When a solution contains no other metal than copper, it may be precipitated in the form of hydrated oxide, by the addition of a proper quantity of pure caustic potash. It is, however, necessary to boil the liquid for some time after adding the precipitant, as also to precipitate from hot solutions; as the hydrated oxide at first thrown down is by this means converted into an anhydrous state, and much more readily freed from any mixture of alkaline salts by subsequent washing with hot distilled water. The oxide of copper thus obtained is afterwards dried in a water-bath, heated to rednesss in contact with air, and then weighed whilst still slightly warm, in order to prevent the result from becoming vitiated by the absorption of hygroscopic moisture. From the quantity of oxide of copper thus obtained, the weight of the metal present is readily deduced, as every 100 parts of this oxide correspond to 79.8 of metallic copper.

Copper is also frequently precipitated from its solutions by passing through them a current of sulphuretted hydrogen gas, by which it is thrown down in the form of a sulphide: this is washed with water holding sulphuretted hydrogen in solution, and after drying on the filter, and roasting off a portion of the sulphur in a porcelain crucible, the residue is dissolved in hydrochloric acid, and the oxide precipitated by caustic potash as above described.

The amount of copper contained in a great variety of ores and mineral substances, of which this metal forms one of the constituents, may be determined with a considerable approach to accuracy by the following process invented by Pelouze.

The substance in which the copper is to be estimated should be dissolved in an acid capable of effecting its complete solution, and an excess of ammonia afterwards added, by which the copper is redissolved with the production of a characteristic blue colour. Into this liquor, whilst in a state of ebullition, a standard solution of sulphide of sodium is poured from a graduated burette, which determines the precipitation of the copper in the form of a dark brown oxysulphide of that metal, having the composition expressed by the formula CuO + 5CuS. If this precipitation be effected with proper precautions, and a little ammonia added from time to time, as the metallic solution nearly approaches saturation, it becomes easy to determine at what precise period the whole of the copper has been thrown down, as the liquor entirely loses its blue colour when the last traces of this metal have been deposited. If the liquor contains no other substance which can be precipitated by the solution of the alkaline sulphide, it will be easy to calculate the amount of copper present from the volume of the solution poured from the gra-

duated burette, as each division of the instrument evidently corresponds to a definite and well-ascertained quantity of metallic copper.

To determine the strength of the test solution of sulphide of sodium, a definite weight, say one grain of perfectly pure copper, should be dissolved in a proper quantity of nitric acid, and to this liquid ammonia is added, until the deposit at first formed has become entirely redissolved, and a bright blue solution, free from all cloudiness, is obtained. Into this liquor the solution of sulphide of sodium is gradually poured from the burette, in which it has been measured, and when the contents of the flask begins to lose colour, it is repeatedly shaken, and again allowed to settle.

At this point of the operation, the liquid from the graduated measure is dropped into the copper solution with the greatest possible caution, in order that the point at which the precipitation ceases to take place may be noted with accuracy. By making two or three experiments of this kind, and taking the mean of the results obtained, it becomes easy to discover to what weight of metallic copper each of the divisions on the graduated burette corresponds, and the data are thus afforded for the determination of the inverse proposition, viz., what quantity of copper is contained in a solution in which the weight of that metal has not previously been ascertained.

If by way of an example we suppose it has been ascertained by direct experiment, that to precipitate from its solution one grain of pure copper, 280 divisions of the burette are required, and that to decolorize a given copper liquor exactly 372 divisions have been employed, it follows that the solution in question contains a

quantity of copper corresponding to  $\frac{372}{280}$  : 1 gr. or 1.32 gr.

This method is also equally applicable to solutions containing other metals besides copper, as experiment indicates that the results are in no way interfered with by the presence of either iron, tin, zinc, cadmium, lead, or antimony, as the alkaline sulphide does not begin to react on these metals until after the whole of the copper has been completely precipitated in the form of oxysulphide. It is, however, absolutely necessary that the iron should be peroxidised by the addition of a few drops of nitric acid, and ebullition, previous to the supersaturation of the liquor by ammonia, as the presence of the protoxide of that metal materially interferes with the result.

On the addition of the ammonia to the liquid to be examined, a deposit of the oxides of some of the other metals which it contains very frequently takes place; but unless these are extremely abundant, they are not found to vitiate the results, and, consequently do not require to be separated by filtration, unless the quantity be so large as to prevent the colour of the liquid from being distinctly seen.

This method of estimating copper is not, however, to be depended on in cases where cobalt, nickel, mercury, or silver are present; but the latter metal may be readily eliminated from the solution by the addition of a few drops of hydrochloric acid, which will cause it to be precipitated in the form of an insoluble chloride, readily removed by filtration.

Copper is separated from the alkalies, earths, manganese, iron, chromium, cobalt, nickel, zinc, titanium, and uranium, by passing a current of sulphuretted hydrogen gas through their solutions, after having first rendered them slightly acid by the addition of hydrochloric acid. The sulphide of copper which is thus obtained is subsequently dissolved in aqua regia, and the metal estimated in the state of oxide, in which form it is precipitated by the addition of pure caustic potash.

Copper may be separated from cadmium, bismuth, and lead, by adding an excess of carbonate of ammonia to their solutions in nitric acid, when the copper alone is redissolved, whilst the other metals will be precipitated in an insoluble form. The same method may be employed for the separation of copper from alumina and the sesquioxides of iron and chromium, but the results obtained by this means are far less satisfactory than those yielded by passing a current of sulphuretted hydrogen gas through the liquid holding the salts of these various metals in solution. The best method of separating copper from lead consists in adding a small quantity of sulphuric acid to the solution of the two metals in nitric acid, and afterwards evaporating the liquor nearly to dryness in a porcelain basin, to expel the excess of sulphuric acid which has been added. The residue is now slightly moistened with nitric acid, and a limited quantity of boiling water subsequently added, by which the copper salt is dissolved, whilst the insoluble sulphate of lead remains in the state of a crystalline powder, which may be readily collected on a filter.

The separation of copper from tin is effected by attacking the alloy by nitric acid, which readily dissolves the first of these metals, whilst the second remains in the form of insoluble stannic acid, from the weight of which the amount of metallic tin originally present in the alloy is deduced.

Copper may be separated from antimony by a similar process, but in this case less accurate results are obtained, on account of the partial solubility of this metal in the solvent employed. The separation of these two metals may, however, be more accu-

rately effected by the use of sulphide of ammonium, as the sulphide of copper thus produced being insoluble in an excess of that precipitant, is readily collected on a filter, and estimated by the method already described, whilst the sulphide of antimony, which is soluble in sulphide of ammonium, is contained in the filtrate, from which it is again precipitated on the addition of a few drops of hydrochloric acid.

## CLASSIFICATION AND ASSAY OF COPPER ORES.

The ores of copper, although extremely numerous, may, for the purposes of assay, be all comprehended under three general classes.

The *first class* consists of such ores as contain, with the exception of iron, no other metal than copper, and which are perfectly free from any admixture of either sulphur, selenium, or arsenic.

The second comprehends those ores which do not contain, besides copper, any other metal except iron, but in which either sulphur or selenium is present in greater or less proportion.

The *third class* is composed of such cupreous minerals as, besides sulphur or selenium, also contain various other metals in addition to iron.

The apparatus best adapted for the assay of copper ores is a small air furnace, very nearly resembling in form and general arrangement that employed in conducting iron assays, and represented at page 212; but as the temperature required to effect the reduction and fusion of the latter is much greater than that necessary to liquefy the former, the size of the fire-place may be proportionately diminished.

For the purpose of assaying copper, a furnace, having a depth of 16 inches from the bars to the level of the fire-tile by which it is closed, will be found amply sufficient; each of the sides of the arrangement may measure from eight to ten inches, and the fuel employed should be good firm coke, broken into pieces a little larger than eggs.

The mass of brick-work in which the fire-place is enclosed is built to such a height from the floor of the laboratory as to admit of the operator being able to observe easily all that is going on within his crucible, and ought either to be well bound together by an arrangement of iron bolts and ties, or be secured from too great expansion by cast iron plates firmly connected together. The chimney must be provided with a damper for the regulation of the draught; and the furnace, when in action, is covered either with a fire-tile or thick cast iron plate. Assay of Ores of the First Class.—When the ores belonging to this class are moderately rich, their assay is attended with but little difficulty, and usually affords satisfactory results. The mineral is first pounded sufficiently fine in a mortar, and, after being well mixed to insure perfect uniformity of composition, is intimately blended with about three times its weight of black flux.<sup>4</sup> The mixture is now placed in a crucible, which should not be more than one-half filled, in order to prevent any loss from the expansion of the pasty mass when strongly heated, and on the top is spread a thin layer of pure black flux, without any admixture of the ore to be treated.

The crucible and its contents are now placed in the furnace, which must be previously lighted for a short time, in order that it may be well heated, and is allowed to remain uncovered until the ore and flux have become reduced to a state of almost tranquil fusion at the bottom of the pot. This usually occurs at the expiration of about fifteen or twenty minutes after the introduction of the assay into the fire, and the crucible is then closed with an earthen cover, and the damper fully opened, so as to subject it during another ten or fifteen minutes to the highest heat of the The crucible is now withdrawn from the fire by means furnace. of proper tongs, and tapped slightly against some hard substance, such as the brick-work of the furnace, in order that any small buttons of metal retained in the slag may fall to the bottom and unite into one solid and well-formed mass: this, when it has sufficiently cooled, is extracted by breaking the crucible.

The quantity of ore operated on for the purpose of assay depends on the richness of the minerals to be treated; but in most instances 200 grains will, for commercial purposes, be found a very convenient amount.

When these ores do not contain a large per-centage of copper, and are consequently much contaminated with earthy and other impurities, it is found extremely difficult to extract the whole of the copper by the method above described, as a large proportion of the metal present is retained by the flux either in a state of chemical combination or as small globules, which are prevented from uniting in a uniform button by the viscidity of the slag in which they are imbedded.

In this case experience has shown that the best results are obtained by adding to the mineral a proper quantity of sulphur, and then fusing for matt in the way shortly to be described with reference to Class 2, and subsequently roasting and fluxing the regulus obtained as though a natural sulphide of copper were

<sup>1</sup> Black flux is prepared by heating together in a large crucible 1 part of nitre and 2 parts of crude tartar.

originally operated on. This method of manipulation has the disadvantage of requiring the expenditure of much more time than the direct fusion of the ore with black flux; but when the mineral treated contains less than from 10 to 15 per cent. of metallic copper, the results obtained by the latter process are found to be much higher than those resulting from the direct fusion and reduction of the mineral in the way usually recommended.

On examining the button obtained by the direct reduction of the various ores belonging to the first class, it will almost invariably be found that they are covered on the surface with a thin layer of matt or regulus produced by the presence of minute portions of sulphur in the original ore; and it is therefore not unfrequently found necessary to subject them to the process of roasting before proceeding to their fusion, with the addition of a proper quantity of some reducing agent, such as tartar or black flux : it consequently follows that in such cases the time occupied by the assay will not be materially prolonged by the previous fusion with sulphur, whilst the result obtained is much more satisfactory. This method, although it at first sight appears extremely rude and unscientific, is nevertheless universally followed by the Cornish assayers, by whose results the price of the copper ores sold in that county are invariably determined. The treatment of the regulus thus obtained will be described when treating of the assay of the different minerals belonging to the second class.

In order to ascertain the amount of copper contained in the slags resulting from the metallurgic treatment of copper ores, it is usual to employ the humid method of determination, as they are commonly too poor to give a distinct button of copper at the temperature of an ordinary assay, and, when too strongly heated, yield an alloy of iron and copper, caused by the simultaneous reduction of the copper and a portion of the protoxide of iron forming one of the essential constituents of these fusible silicates.

When slags are readily acted on by acids, they should, after being properly pulverised and passed through a fine lawn sieve, be attacked by hydrochloric acid, or, if this reagent be not sufficiently powerful, by strong aqua regia. After having heated the flask in which the attack is being made until all chemical action appears to have ceased, its contents are carefully transferred into a porcelain evaporating basin, where they are reduced to dryness for the purpose of rendering the silica completely insoluble. The residue is now first moistened with hydrochloric acid, which is afterwards diluted with water, and the soluble portions separated from those which are not dissolved by filtration. The filtrate obtained contains the whole of the copper present in the substance, and which, with proper precautions, may be estimated either by precipitation with a bar of iron or zinc, by sulphuretted hydrogen, or by the method of Pelouze.

Assay of Ores, &c. belonging to the Second Class.—The minerals belonging to this class are either sulphides or sulphates, and may occasionally contain selenium.

Fusion for Regulus or Matt.-This operation is extremely simple, and consists in strongly heating the ore with substances capable of determining its fusion, and the separation of its earthy impurities or gangue, together with the elimination of a portion of its sulphur. These conditions are better fulfilled by a mixture of nitre and borax than by any other flux, as, with a proper quantity of these reagents, all the ores belonging to the second class are readily fused at a dull red heat, with the production of a vitreous slag, and the formation of a neat and well-defined button of matt at the bottom of the crucible. For this operation naked pots are usually employed, and the button is obtained by breaking the crucible after it has been allowed to cool. Great precaution is, however, necessary in this case to enable the whole of the matt being collected without loss, as it is exceedingly brittle, and is liable to adhere somewhat firmly to the sides of the pot, from which it is not readily detached. This inconvenience may be avoided by the use of a lined crucible similar to those employed in the assay of iron ores; but in my own practice I have invariably found it much more convenient and expeditious to effect the fusion in a common earthen pot, and, when the contents are in a perfect state of fusion, to pour them rapidly into a cast iron mould having interiorly an elliptical form.

By operating in this way, the earthen pot is not only economised as being preserved for several successive fusions, but the button found at the bottom of the mould is, with its adhering slag, readily removed, when cold, by turning it over and giving it two or three smart taps against some hard body. The subsequent separation of the regulus from the vitreous scoriæ above it, is easily effected by the use of a small chisel-edged hammer; and a sheet of brown paper should be placed beneath the button whilst being thus detached, in order to collect any fragments of the sulphide which may be accidentally broken off.

When extremely poor ores are operated on, it is advisable to employ a lined crucible, but in all other cases this is by no means requisite.

The regulus thus produced consists of sulphides containing a small amount of sulphur only; and, as the ores of copper are composed of the higher sulphides, it follows that a certain portion

of the combined sulphur has been removed during the process of fusion, and, consequently, the difference between the weight of the ore originally operated on and that of the button of matt found, will not represent the weight of gangue with which the mineral was originally associated.

Assay for Copper.—To obtain copper from the ores of that metal containing sulphur, it is necessary that this substance should be expelled by roasting, before attempting to reduce the copper to the metallic state by deoxidising fluxes. It is also of the greatest importance that this elimination should be most completely effected, since, if any traces either of sulphur or sulphuric acid were allowed to remain, the slags would retain a portion of copper, and the results be considerably vitiated.

When the ores are moderately rich, and produce from 20 to 35 per cent. of metallic copper, the roasting and subsequent reduction of the metal may be made either directly on the ore itself or on the matt obtained from the fusion for regulus. In the case, however, of poor ores, such as those of Cornwall, which only contain from 8 to 10 per cent. of metal, it is far better first to obtain a button of regulus by the process described in reference to the poorer minerals belonging to the first class, and afterwards treat this for the copper which it contains by subsequent roasting and reduction.

If these poor ores were directly roasted and reduced, the large quantities of earthy impurities present would be found to interfere materially with the expulsion of the sulphur, both by mechanically protecting it from the action of the air, and also by affording other bodies with which it may form new combinations and give rise to various sulphides and sulphates.

In the fusion of calcined ores with reducing flux, the presence of large quantities of earthy impurities is also extremely prejudicial to the success of the operation, as the slags produced are thereby rendered infusible and viscid, and, consequently, retain portions of the metal both in a combined state and in the form of minute globules, which are unable, from the impermeability of the mass, to fall down and collect in one button at the bottom of the crucible.

The roasting of the ore or fused regulus is conducted in the same crucible in which its subsequent fusion with the reducing flux is to take place, and, at the commencement of the operation, care is to be taken not to agglutinate the pounded sulphide by the application of too strong a heat. To conduct this operation with certainty, the ore or regulus should be first finely powdered in an iron mortar, and then placed in an earthen crucible, which is arranged in an inclined position on the coke of a furnace, of which the draught should be almost entirely cut off by the damper. A very moderate heat is by this means obtained, and the ore must be kept continually stirred with a slender steel rod, so that every particle may have been in its turn exposed to the oxidising influences of the atmosphere. When a certain portion of the sulphur has been thus eliminated, and a corresponding quantity of oxide formed, the crucible may be without inconvenience heated to redness.

At this stage of the operation it is found advantageous to heat from time to time the half-roasted mass to full redness, as by this treatment the sulphides and sulphates are reduced to the state of oxide through the elimination of the sulphurous acid which is generated by their mutual reaction.

When sulphurous acid is no longer evolved, and the process of roasting is consequently far advanced, the heat should for some minutes be raised to whiteness, in order to decompose the sulphates; and after this is effected, the crucible is withdrawn from the fire and allowed to cool.

To reduce the roasted ore to the metallic state, it must be intimately mixed with from three to four times its weight of black flux, and, after being again placed in the crucible in which the roasting was effected, and covered with a layer of about half an inch of fused borax, its fusion is accomplished by exposure during twenty minutes to the heat of a small wind furnace.

Instead of simply fusing with the addition of black flux and borax, the contents of the crucible may be intimately mixed with a fourth of its weight of lime, from 10 to 20 per cent. (according to the richness of the ore) of finely powdered charcoal, and one and a half times its weight of soda-ash: this mixture, when intimately blended, is introduced into the crucible in which the ore was roasted, and, after being slightly pressed down, is covered with a layer of about 100 grains of dried borax.

The open crucible, when thus prepared, is introduced into the fire, and exposed during a quarter of an hour to a red heat. At the expiration of this time the intumescence of the contents of the pot will have entirely ceased, and it must now be covered with an earthen lid and exposed to a bright red heat bordering on whiteness for another quarter of an hour. The reduction and fusion of the ore will be now fully effected, and the crucible and its contents must be removed from the furnace by the use of proper tongs.

To obtain the button of metal, the contents may be either rapidly transferred into the mould before described, or if it be preferred, the crucible can be allowed to cool, and being afterwards broken, the slag and other adhering substances may be removed with a hammer.

In most instances the roasting of minerals belonging to this class may be conducted without difficulty, as the only care necessary is to prevent the agglutination of the particles by the application of too strong a heat at the commencement of the operation. If, however, the button obtained has not a bright metallic surface, but is covered with a layer of matt of a greater or less thickness, it is sufficient evidence that the whole of the sulphur has not been expelled, and consequently that another assay, preceded by a more careful roasting, must be made.

To assist in the elimination of the last traces of sulphur, which in the form of sulphate is apt in some instances to be retained with considerable obstinacy, Mr. Mitchell recommends that at the close of the operation, and whilst the crucible and its contents still remain red-hot, a quantity of pulverised carbonate of ammonia, equal in weight to one-tenth the total quantity of ore employed, should be gradually and carefully added, and thoroughly incorporated by stirring, with the roasted mineral.

By this treatment the various sulphates formed are readily decomposed with formation of sulphate of ammonia, which, being a volatile salt, is at once carried off in the state of vapour, and every trace of sulphur completely removed.

This injection of carbonate of ammonia into the pot is, however, attended with inconvenience, as the rapid evolution of vapour which takes place on its coming in contact with the highly heated ore, invariably causes a considerable loss, by carrying off with it some of the mineral in a finely divided state; and it is therefore generally best not to have recourse to this salt, particularly as with proper care the whole of the sulphur may be entirely eliminated by the alternate heatings and roastings already described.

The sulphates of copper are completely decomposed by heat, and are therefore readily assayed, by first driving off the sulphuric acid by heating to whiteness in an earthen crucible, and subsequently fusing the residue in the same pot with a due admixture (say three parts) of black flux. Instead of black flux, the mixture of lime, charcoal, carbonate of soda, and borax, described with reference to the roasted sulphides belonging to this class, may be employed.

The sulphates of copper, being soluble salts, are very readily assayed by the wet way, as they may be at once dissolved in water, and the metal thrown down from the filtered liquid by the introduction of a bar of either iron or zinc. The resulting metallic copper, after being washed in dilute hydrochloric acid to remove any adhering subsalt of iron, if the precipitation has been effected by the use of that metal, may, when thoroughly washed, be either dried at a low temperature, and weighed as metallic copper, or be estimated as oxide after being carefully roasted with free access of air.

Assay of Ores of the Third Class.—The minerals belonging to this class are to be treated in a similar way to those of the second, but the preliminary roasting will, from the great fusibility of these ores, require to be conducted with some precaution, and the button obtained by the reduction of the calcined ore, instead of being, as in the former cases, pure copper, will consist of an alloy of that metal with the other metallic substances.

When the ore contains lead, the process of roasting must be conducted with the greatest care, as it is then extremely difficult so to moderate the heat as to expel the arsenic and sulphur, and at the same time prevent the agglomeration of the powder.

In every instance the assay of minerals belonging to this class should be commenced by a fusion for matt, as by operating in this way the sulphides are not only reduced to a minimum state of sulphuration, but a very large proportion of the associated arsenic is also driven off.

When an ore contains an arsenide of copper, a certain portion of arsenic is evolved during the process of roasting, and copper, oxide of copper, and arseniate of copper, are the first results. On being strongly heated, the arseniate of copper formed, and the undecomposed arsenide, react on each other, and arsenious acid is evolved. When, however, the whole of the arsenide present has been decomposed, no further elimination of arsenic can be so effected, and it becomes necessary to heat the half-roasted ore to bright redness, with the addition of powdered charcoal, which again gives rise to the expulsion of a fresh portion of arsenious acid, produced by the deoxidation of the arseniates formed.

By repeatedly acting in this way, a very large proportion of the arsenic present may be got rid of, but a small quantity will invariably be retained in the mixture, and contaminate the button of copper resulting from its subsequent treatment.

The purification of the alloy obtained is now to be effected by a process called refining. This operation has for its object the separation of all the more oxidisable metals with which the copper is associated, and is carried on in an ordinary muffle furnace. As a support for the button of alloy, a bone-ash cupel is often employed, and as a considerable degree of heat is required, the furnace should have a good draught. When the furnace and cupel have become heated to bright redness, the button of impure copper is introduced with proper tongs, and the opening of the muffle closed during a few minutes with its stopper, in order to exclude the air, and cause, by the temporary elevation of temperature, the fusion of the metal.

When the button has become melted, and the door has been again removed from the mouth of the muffle, the addition of a little pure lead is made to the fluid alloy, and the operation of refining at once begins. The lead, the combined metals, and a portion of the copper itself, are thus oxidised, and form a fusible compound which surrounds the central globule of metallic copper, and is gradually absorbed: the button now appears to be agitated by a rapid rotatory motion, and is constantly covered by a brilliant iridescent pellicle. At the point at which the process of refining is about to terminate, this movement becomes more rapid, and the colour of the coating of oxide grows brighter, but the button of metal soon becomes suddenly consolidated, and the pellicle of oxide at the same time entirely disappears.

These appearances constitute what is called the brightening of the button, which, with the cupel on which it is supported, may be at once removed from the muffle.

The refined metal, when taken from the cupel, is invariably covered with a coating of oxide, which is extremely difficult to remove when the cooling has been allowed to take place gradually, but if, on withdrawing the button and its support from the furnace, they be immediately plunged into water, the oxidised coating becomes so far detached as to admit of being easily removed by a few blows of a light hammer.

The cleansing of the refined metal is still further facilitated by throwing on the button, immediately after it has brightened, and before removing it from the muffle, about seven per cent. of vitrified borax, in fine powder. The covering of fused borate of soda with which it is in this case covered, will be found extremely brittle, and but slightly attached to its surface, as the first blow of a hammer is, in most instances, sufficient for its removal. The same results may be obtained by plunging the button, whilst red hot, in a weak solution of phosphate of soda. The resulting copper, if perfectly refined, should be very malleable, and have a full-red colour.

The per-centage amount of copper contained in the button of alloy cannot, however, be directly deduced from the weight of refined metal obtained, as a portion of copper is not only carried off in the state of oxide with the lead and other metals, and consequently absorbed in the cupel, but a certain quantity is likewise expended in the formation of the coating of oxide or borate with which its surface is invariably covered. With regard to the copper ores thus treated, two distinct cases may occur; they may either contain lead, or be entirely free from all mixture of that metal. When none is present, a tenth part of lead is added, in successive portions, until the copper be pure. To determine the true proportion of copper contained in the alloy, Berthier recommends that one-eleventh of the weight of all oxidisable metals, including the lead added, and one-tenth of the weight of the borax thrown on the cupel, should be added to that of the assay button obtained. This, however, though sufficiently near the truth for many practical purposes, cannot be rigorously exact, as the loss experienced must depend, not only on the amount of oxidisable metals present, but also on the nature of these metals, and the degree of heat to which the button may have been subjected during the process of refining.

When copper is associated with lead, it may either be present in too small proportion for the purposes of refining, or may be sufficient, or too much, for immediate treatment on the cupel. In the first case lead must be added by tenths, until the copper remains pure; in the second it becomes unnecessary to make any addition; and in the third instance a weighed quantity of fine copper must be supplied; after which the assay is conducted with the usual precautions, and the ordinary deductions and allowances made.

The proportion of copper contained in a button of alloy, can, however, be at once determined, without making any of the suppositions which are necessary by the method already described; and this mode of operating is consequently in some instances to be preferred, particularly when the alloy examined already contains lead, as in such cases it is requisite to determine, with at least a tolerable degree of approximation, the amount of that metal, before being enabled to allow for the loss experienced by the copper.

To obviate this inconvenience, two cupels should be placed side by side in a well heated muffle, and when sufficiently hot, an equal quantity of pure lead, say 400 grains, is to be introduced into each. As soon as this has become melted, and presents a bright even surface, 100 grains of pure copper are added to the one, and an equal weight of the alloy to be examined to the other.<sup>1</sup>

The refining is now conducted in the usual way, and on weighing the resulting buttons, that from the pure copper will be found to be the heavier. If, then, we allow, which must be very nearly the case, that the difference between the two weights corresponds to the quantity of foreign metal contained in the alloy, and that the actual quantity of copper oxidised is the same in both instances, it follows that by adding to the weight of the button obtained from the alloy, the loss experienced on the pure copper, we shall at once obtain the total quantity of copper originally contained in the mixture.

<sup>1</sup> The Cornish assayers invariably refine the button of reduced copper obtained by a second fusion with a mixture of 2 parts of nitre and 1 part of common salt.

This assumption, though not in all cases strictly correct, is sufficiently exact for commercial purposes, and affords good data by which to calculate the amount of copper which could be extracted from such alloys by ordinary metallurgic treatment. The process of refining will in every respect be precisely the same, whether the metal treated be an artificial alloy, or the product of the immediate reduction of the roasted ores belonging to the third class; and when the process last described is employed, there is no inconvenience in the use of a large excess of lead on the cupel.

Estimation of Copper by the Wet Way.—To assay copper ores by the humid way, they should, after being properly pulverised, be treated with aqua regia diluted with water, and the liquid supersaturated with ammonia, and filtered. The precipitate must also be washed with ammonia, until the drops passing through the filter have become perfectly colourless, after which the filtrate must be evaporated to dryness, to expel the ammoniacal salts, and the fixed residue dissolved in hydrochloric acid, from which solution the copper is precipitated by a plate of iron or zinc, and estimated with the precautions already detailed.

Should the mineral operated on be suspected to contain silver, it becomes necessary to filter the solution in aqua regia, before the addition of ammonia, by which the chloride of silver, if any were present, would be readily dissolved, and either cause an explosion on evaporating to dryness, or be reduced together with copper to the metallic state, on the introduction of the bar of iron or zinc.

## METALLURGY OF COPPER.

The ores most frequently treated for copper are the sulphides, and of these, copper pyrites is by far the most abundant and important. Copper glance and grey copper ore are also abundantly found in some localities, and are valuable sources of this metal.

The grey ore, or Fahlerz, in many instances contains silver, and is on that account subjected to various processes in order to effect its separation.

The oxides and carbonates are of more rare occurrence, and are for this reason less extensively employed for smelting purposes; but contain a much larger per-centage of metal, and are consequently valuable in the same proportion. These ores (the oxides and carbonates) afford the metal which they contain with great facility, and therefore admit of very simple metallurgic treatment. By simple fusion in a small blast furnace with a due admixture of siliceous slags, they yield a metallic alloy known by the name of black copper, and which, after being subjected to a process of refining, is converted into the ordinary cake copper of the markets.

The sulphides of copper are, on the contrary, extremely difficult to reduce, and require several preliminary roastings before this can be effectually accomplished. The object of this is to transform a large portion of the sulphides present into oxides by the oxidising influence of the air. The roasted ores are afterwards fused, either with siliceous matters, used as a flux, or with other ores containing a proper amount of silica, in a reverberatory furnace or cupola, by which means a liquid matt, rich in copper, and containing a smaller per-centage of sulphur than the original ore, is obtained.

Copper, when thus treated, has a stronger affinity for sulphur than the iron with which it is associated ; whilst, on the contrary, the latter very readily combines with oxygen, particularly in the presence of silicic acid, by combining with which various silicates of the protoxide of iron are produced. The oxide of copper formed during the process of roasting is, from this cause, entirely converted into sulphide, at the expense of the sulphide of iron and fusible silicate of that metal, and a fluid matt, rich in copper, is the result of the operation. The siliceous slag thus contains the greater portion of the iron originally present in the pyrites, and the matt produced consists of nearly the whole of the sulphide of copper, together with traces of sulphide of iron which have not been entirely decomposed. This product is again subjected to a further roasting, and is subsequently fused either with siliceous matter, or with a natural carbonate or oxide of copper containing a proper amount of silica. By these means another slag is obtained at the expense of the greater portion of the iron contained in the first matt, whilst that which is now produced is still richer in copper than that resulting from the first fusion of the ore. These operations are successively repeated until an impure black copper is produced, together with a certain portion of very rich matt and a fusible slag. The matt thus obtained is added to that produced in other operations, and consequently the final result will in all cases be black copper, which is afterwards rendered ductile and malleable by being subjected to a process of refining.

The details of the processes by which copper is obtained from its ores vary exceedingly in different localities, and it would, therefore, be impossible, within the limits of the present Treatise, to describe the whole of them with any degree of exactness; I shall therefore confine myself to some of the more important methods, which may, at the same time, be considered as types of the various classes to which they belong.

## ENGLISH METHOD OF COPPER-SMELTING.

In this country, where more than one-half of the copper consumed in the world is annually produced, a very complicated system of metallurgic treatment is adopted.

The most important mines of Great Britain are those of the county of Cornwall, and the principal establishments for the metallurgic treatment of copper ores are situated in the neighbourhood of Swansea, in South Wales. These smelting works, besides reducing the ores obtained from the mines of the West of England, are also furnished with a considerable annual supply from various other countries; such as South Australia, Chili, Peru, and the Island of Cuba.

The minerals treated in this locality may be divided into various classes in accordance with their respective richness in copper and the nature of the substances with which the metal is associated.

The 1st class consists of copper pyrites mixed with large quantities of iron pyrites, and accompanied with but a very small amount of either oxide or carbonate of copper. The gangue usually contains much earthy and siliceous matters; the percentage of metals varies from 3 to 16 per cent.

2d Class.—Copper pyrites having nearly the same chemical composition as the minerals of the above class, but much richer in copper. These ores may contain from 15 to 25 per cent. of metallic copper.

3d Class.—Copper pyrites containing but a small proportion of iron pyrites, or any ingredient liable to deteriorate the quality of the metal produced, but a larger amount of the various oxidised ores of copper.

4th Class.—Minerals chiefly composed of the oxides and carbonates of copper mixed with variable proportions of the sulphuretted ores of the same metal. These minerals, which are usually associated with quartz, contain from 20 to 30 per cent. of pure copper.

5th Class.—Oxidised minerals, extremely rich, free from sulphur and all substances exerting a pernicious influence on the quality of the metal obtained. These ores frequently contain above 80 per cent. of copper, which exists either in the metallic state or as a mixture of the carbonate with the red oxide. These choice minerals are associated with a siliceous gangue, and are chiefly brought either from Chili or South Australia.

The details of the different operations employed for the reduction of copper ores by the Welsh method are sometimes slightly varied so as to suit the peculiarities of the various ores treated ; but M. Le Play, who has closely studied the fabrication of this metal in the smelting establishments of Swansea, is of opinion that the whole of the manipulations practised in the works of that district may be comprehended under the ten following processes :---

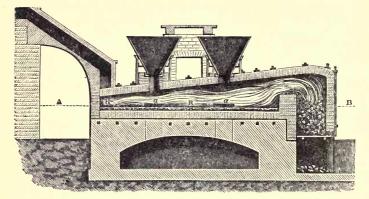
I.-Calcination of ores of the first and second classes.

- II.—Melting for coarse metal, or fusion of the roasted ores with minerals of the third class not calcined.
- III.-Calcination of the coarse metal.
- IV.—Melting for white metal, or fusion of the coarse metal, with the addition of rich minerals belonging to the fourth class.
  - V.—Melting for blue metal, or fusion of the calcined coarse metal with roasted minerals moderately rich in copper.
- VI.—Remelting of slags, or fusion of the rich slags obtained from the operations IV. VII. VIII.
- VII.—Roasting for white metal, or production of white metal of extra quality. This operation sometimes includes the roasting of the blue metal obtained in process V.
- VIII.—Roasting for regulus, or preparation of extra white metal.
  - IX.—Preparation of crude copper by the roasting and fusion of ordinary white metal, regulus, &c.
    - X.—Refining and toughening of the crude copper, and production of malleable metal.

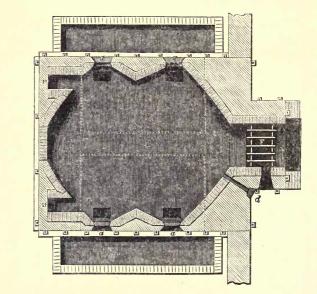
I.—The metallurgic treatment of the ores of copper commences by roasting minerals belonging to the 1st Class in a reverberatory furnace, of which fig. 145 represents a vertical, and fig. 146 a horizontal section made in the direction of the line  $\land$  B. The hearth, or laboratory of this furnace, B, which is 16 feet in length and 13 feet 6 inches in width, is formed of refractory bricks set on edge, and firmly bedded in fire-clay. The arch descends rapidly from the fire-place, F, to the flue-holes, H, by which the gases of the furnace escape through a proper flue into a high chimney. A current of cold air is admitted into the apparatus by an aperture, d, which admits of being either partially or entirely closed by a damper sliding in a groove.

The two opposite sides of the furnace are placed on a level with the hearth, with four rectangular openings or doors, a, immediately before which, in the floor of the laboratory itself, are situated four openings, e, of nearly the same size and form as the working doors of the furnace. During the time this apparatus is in action these are closed by iron plates, which are removed at the close of each operation in order to allow the roasted charge being raked through them into the arched chambers, c, immediately beneath.

The arch of the furnace, the mean height of which, from the hearth, R, is two feet, supports two large hoppers of sheet iron, s, in which is placed the mineral afterwards to undergo the process



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of roasting. These spouts are provided with sliding doors at their lower extremities, by the withdrawal of which the ore may be made to fall directly on the bottom of the arrangement.

The combustible employed in the Welsh Copper Works is the anthracite found in that district, which ignites with considerable difficulty, and is liable, under the influence of heat, to divide into extremely small fragments. On this account, if consumed on an ordinary grate, the fire would soon become choked from the accumulation of fine dust, by which the draught becomes obstructed. The flame obtained from this substance under ordinary circumstances would, moreover, not be of sufficient length to heat in a uniform manner, in its whole extent, the hearth of the furnace.<sup>1</sup>

Both these inconveniences are, however, perfectly obviated by a very simple and ingenious contrivance, by which the fuel is consumed on a grating so constructed as to supply it constantly with the amount of heated air necessary for its combustion. The anthracite, in burning, leaves a proportion of earthy matter, which, at a high temperature, is readily fused into a siliceous slag, and with this the smelter forms a kind of hollow grate, which is supported by a few bars of iron placed at considerable distances from each other. To prepare a grating of this kind some large fragments of scoria are so placed on the bars as to form a first layer, and on this the ashes of the combustible are allowed to accumulate in proportion as they are produced : by the fusion of these cinders numerous fragments of anthracite become imbedded and agglutinated together, and a kind of spongy siliceous mass, traversed by a great number of apertures, is the result. When these matters have, through repeated accumulations, become raised to a sufficient height from the bars, their further increase is prevented by occasionally causing the fall of the lower portions by the use of a long bar of iron. In this way is formed, through the earthy mass, a sufficient number of channels to yield a free passage to the air necessary for the combustion of the fuel, and which, in passing through the interstices of the heated slag itself, acquires a considerable elevation of temperature; these apertures, although sufficiently numerous for the passage of air, are too small to allow the finely-divided anthracite to descend into the space beneath the bars. The anthracite used for fuel is mixed with about one-fourth part of its weight of the screenings of a caking, bituminous variety of coal, which serves to bind together the combustible, and impart to it the necessary degree of porosity.

The air passing, by an almost infinite number of channels, through the stratum of anthracite thus arranged, is principally converted into carbonic oxide gas, which, together with the nitrogen result-

<sup>&</sup>lt;sup>1</sup> Le Play.

AA

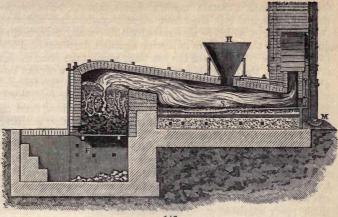
ing from the decomposition, passes over the fire-bridge into the laboratory of the furnace. Here it takes fire, and is consumed at the expense of the atmospheric air which enters by the opening, d, as well as by various small holes left in the iron plates, by which the lateral openings are closed during the roasting. In this way the whole internal cavity of the furnace is constantly occupied by a long sheet of flame, caused by the ignited carbonic oxide gas, which burns on coming into contact with a stratum of atmospheric air so admitted as to spread immediately over the surface of the hearth. The minerals spread on the sole are consequently exposed to a current of air, above which is a parallel sheet of carbonic oxide gas, which is inflamed at its lower surface, where it comes in contact with the oxidising stratum, and thereby affords the amount of heat necessary to carry on the operation.

The working of a charge of ore commences without any interval in the action of the furnace, and is begun immediately after the withdrawal of the calcined ore resulting from the preceding shift. Each charge varies in weight from three to three and a half tons, and is introduced by withdrawing the sliding dampers from the bottom of the hoppers, in which the ore is placed during the working of the preceding parcel. As soon as it has been let down, it is spread evenly over the surface of the hearth, by long iron rakes, successively introduced through the four working doors, which are securely closed immediately that the bottom of the furnace has been properly covered. At the expiration of two hours these are again removed, and the ore is stirred with long iron bars, in order to expose a new surface to the oxidising influences present.

This operation is repeated at intervals of two hours, and after the expiration of twelve hours the roasting is considered to be sufficiently advanced. In order to withdraw the charge, the workmen open the four working doors, a, and after having removed the plates of iron which cover the openings, e, draw the mineral through the apertures by the use of iron rakes, and cause it to fall into the arched chambers, c, from which, when sufficiently cooled down, it is removed in order to be charged in the fusing furnace of the next operation.

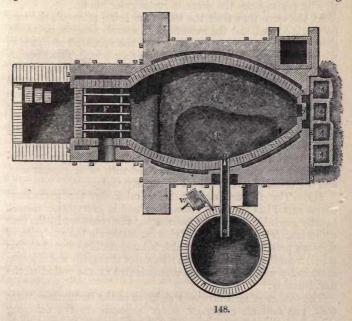
II.—This furnace is represented by figs. 147 and 148, of which the first is a vertical, and the second a horizontal section. The fuel employed for the fusion of the roasted ore consists of a mixture of two-thirds of anthracite, and one-third of caking coal screenings, which, as in the former case, are burned on a layer of slag supported on iron bars. The heat in this instance also is produced by the combustion of carbonic acid gas, but a much higher temperature is attained by a considerable increase of draught. The sole, s, is composed of vitreous slags, and is so lowered at the

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point, B, as to afford a kind of internal basin. To form a charge



for this furnace, a certain amount of raw mineral, belonging to the 3rd Class, and rich slags from other operations, are added to the roasted ore, which is also mixed with a small proportion of fluor spar, for the purpose of imparting a greater degree of liquidity to the scoriæ. By means of the reactions which take place in this arrangement, the copper is made chiefly to combine with the sulphur, whilst the iron, uniting with oxygen, is, in the form of variously composed silicates, carried off in the slags produced. In addition to this, the oxides and sulphides are made to react on each other, and by this means the elimination of a further quantity of sulphurous acid is determined.

This operation occupies four hours, and the products consist of a matt containing the greater proportion of the copper in the state of sulphide, combined with a certain quantity of sulphide of iron, and a slag extremely rich in oxide of iron, and containing numerous disseminated fragments of quartz, which gives to the whole a thick pasty consistency. These slags are removed by an iron rake, through the door, *d*, placed at the end of the furnace, opposite the grate, from whence it falls into a series of sand moulds, M, where it assumes the shape of rectangular bricks.

At the same time that the scoriæ are being removed, the taphole, a, is opened, and the matt flows in a small continuous stream through the cast iron channel, a, a, into the vessel full of water, v, where it becomes divided into shot-like fragments. These granulations are collected in a perforated wrought iron pan, which, after the cooling of the matt, is withdrawn by the aid of the winch, w. This matt, which is known by the name of coarse metal, contains, on an average, about 35 per cent. of metallic copper.

The scoria resulting from the foregoing operation are broken with a heavy hammer, and subjected to a careful examination.

Those which contain a considerable amount of copper are preserved for the purpose of being remelted with other roasted ores, and the remainder are rejected as entirely useless.

III.—The furnace employed for calcining the granulated coarse metal has the same dimensions, and in every other respect exactly resembles that used for roasting the crude ore in the first operation. The chief object of this calcination is the oxidation of the iron present in the matt, which is more readily effected at this stage, from the almost complete removal of the earthy and siliceous matters by which the ore was contaminated at the period of the first roasting.

The charge of each furnace weighs, as in the former case, three tons, and requires thirty-six hours' exposure to the oxidising influences of the heated gases, before its calcination has become sufficiently advanced. During this time the matter on the floor of the furnace is frequently turned with an iron rake, and at the termination of the process it is drawn through an opening, and falls into a chamber, by the arched roof of which the hearth of the arrangement is supported.

IV .- The roasted coarse metal is melted with a due admixture of minerals belonging to the fourth class: i.e. with such as contain but a small proportion of iron pyrites, and are rich in oxide and carbonate of copper. To this is added some rich copper slag, obtained from the process of refining to be hereafter described, and a small proportion of the scales which fall from the rollers by which the metal is reduced to the state of sheet copper. The furnace in which this fusion is carried on nearly resembles that in which the calcined ore of the first operation is melted, but is without the internal basin there described. The method of regulating the fire is also precisely similar, but in this case it is sought to produce a higher degree of heat, and the operation occupies a longer time by an hour than the fusion for coarse metal already described. For this fusion the charge should be so arranged that the whole of the sulphide of iron present may become oxidised at the expense of the metallic oxide, and in the form of a silicate pass directly into the slags; whilst on the other hand the copper combines with the sulphur to form a fusible sulphide. These reactions principally take place after the matters constituting the charge have entered into a state of complete fusion, and appear to be almost entirely limited to the mutual reaction of the sulphide of iron and oxide of copper, as a very small quantity only of sulphuric acid is generated and evolved. Towards the close of the operation, the workman stirs the charge briskly with an iron paddle, and afterwards urges the fire during a short time, in order to insure a proper separation of the fusible matt from the slag with which it is associated. The tapping-hole is now unstopped, and the liquid matt, or white metal, flows into sand moulds, where it assumes the form of rectangular cakes. These operations occupy from five to six hours, and the scoriæ which follow the sulphides, in flowing from the furnace, are divided by careful hand-picking into two classes. Those which are rich in metal are selected for separate treatment, by which copper of a superior quality is obtained, whilst those of a poorer description are reserved to be mixed with the roasted coarse matt in the next fusion.

The sulphide thus obtained, to which the name of white metal is given, contains about 70 per cent. of metallic copper, and is very nearly represented by the formula CuS, although in almost

every instance it still retains variable small quantities of sulphide of iron.

V.—The manipulations employed to effect the Vth operation, are in general extremely analogous to those already described, and in many points of view they may be regarded as almost identical with those of the fusion IV. A similar observation may be made with regard to the three succeeding operations. The VIth melting in all its principal details resembles the operations IV. and V., whilst the VIIth and VIIIth operations are in reality but modifications of the IXth stage of this complicated process.

The fusion V., and the roasting VII. and VIIÎ., which are complementary to each other, are made with a view to the preparation of a matt of richer quality, and, above all, containing less impurities than the ordinary white metal of the operation IV. This object is effected by producing, by successive operations, various reactions of a more varied and efficacious nature than those which, under ordinary circumstances, are accomplished by a simple fusion. For this reason, these three operations are, in the Welsh smelting establishments, grouped under the name of the *extra process*, in contradistinction to the *ordinarg process*, of which IV. forms one of the connecting links.

These two divisions of the routine employed for the treatment of copper ores in the Welsh smelting works, are, however, intimately connected with each other in three distinct points of view. In the first place the raw material used is the same in each case, viz. the roasted coarse metal; their final products are moreover all subjected to the IXth operation; and lastly, one of the accessory products of the fusion IV.—*i. e.* the richest slags produced in this stage of the manipulation—when subjected to the VIth fusion, give rise to the formation of matts, which are subsequently treated in the operations VII. and VIII. in the same way as the blue metal of the Vth process. These two series of manipulations are consequently directly connected by the fusion VI., and for this reason it has been thought proper to introduce the description of the extra process in the order which it occupies in the tabular synopsis.

In another point of view a considerable difference exists between these two branches of the Welsh method, as the products of the extra process derive their superior quality, not only from the greater care employed in their treatment, but also in a certain degree from the more careful choice of the ores. The roasted coarse metal used for the fusion No. V. is consequently sometimes prepared from carefully selected ores, or, when this is not the case, addition is made of a certain portion of roasted pyrites of the purest description belonging to Class 2. The furnace in which this first operation of the extra process is conducted, exactly resembles that used for the IVth fusion, and the combustible with which it is supplied is also the same. Twenty-two charges of 2 tons each are usually passed through the furnace during each week.

The characteristic reactions of this fusion are analogous to those of the preceding operation. The first application of heat determines the liquefaction of the sulphides, and a partial reaction between them and the oxides also present in the mixture constituting the charge. The oxide of copper, in particular, reacts by means of its oxygen on the sulphur and iron of the mixed sulphides, giving rise to the formation of sulphurous acid, which is evolved in the gaseous state, and protoxide of iron, which combines with silica to form a fusible slag : the copper which is thus set free combines with the undecomposed matt, which is enriched by the double channel of the accession of a fresh amount of metal, and also by the elimination of a certain proportion of the sulphide of iron with which it was associated. During the time that these reactions are proceeding, a silicate, to a greater or less extent charged with oxide of copper, begins in its turn to enter into fusion, and at this period commences a kind of slow refining during which the oxide of copper of the silicate, and the sulphide of iron of the matt, produce by their mutual reaction, and without any evolution of sulphurous acid gas, a certain amount of sulphide of copper, by which the matt is enriched, while oxide of iron, which passes directly into the slags, is separated.

VI.-The furnace employed for this operation is, in the interior, formed precisely in the same way as the furnaces used for the other fusions already described; but from the mechanical difference which exists between the substances treated, it becomes necessary that some slight variations should be made in its external arrangement. The scoriæ which are introduced in the form of large fragments, could not be conveniently charged by the iron hoppers hitherto employed for that purpose, and these are consequently suppressed in the furnace devoted to the VIth operation. On the other hand, it would be extremely difficult to spread them equally over the whole surface of the hearth, by charging through the door situated at the farthest extremity of the furnace, and therefore an opening is so placed in one of the sides, as to facilitate this operation. The lateral door is only opened during the time the charge is being introduced, and is hermetically sealed with a luting of fire-clay during the whole period of working it off. The embrasure in which the tappinghole is situated is invariably on the opposite side of the furnace, at the other extremity of the smaller axis of the hearth.

Each charge consists of two tons of different products containing copper, of which the greater portion consists of slags from the operations IV. VII. and VIII., to which are added various small quantities of sweepings from the smelting-house floors, and siliceous ores in which the metal occurs in the form of copper pyrites. The working of each charge occupies  $5\frac{1}{2}$  hours, and the fuel employed is a mixture of anthracite and common coal, in the proportion of three parts of the former to one part of the latter. The object of this operation is the production of a richer matt than that obtained from the preceding fusion, and this is effected by the mutual reaction of the oxide of copper, of the slags, and a matt, of which the elements are derived either from the small metallic globules mechanically mixed with the scoria, or from the very pure sulphides of iron and copper furnished by certain chosen varieties of minerals.

This reaction, the nature of which has been already explained, would of itself merely produce a rich matt, but the smelters have discovered by experience that its quality is materially improved by the precipitation at the same time of a certain quantity of metallic copper, and for this reason they throw into the furnace a little finely divided pit coal, by the action of which on the oxide of copper present, a small amount of metallic copper is produced. The copper thus revived traverses both the slag and the matt, on which it floats, and collects beneath the latter in two distinct layers. The lower of these consists of impure black copper, called by the workmen *bottoms*, whilst the other is composed of an impure white alloy, chiefly composed of copper and tin, and known by the name of *hard metal*.

The mineral added to the charge is commonly copper pyrites, free from all substances liable to injure the properties of the copper produced, and which, from the large quantity of quartz which it contains, would be too poor to be introduced after roasting, into the fusion No. V.

VII.—The object of this operation is to convert the blue metal into white metal analogous to that produced by the fusion IV., and to expel, in a more effectual manner than is usually done in that stage of the process, the different substances injurious to the quality of the copper. This is effected by two successive reactions, viz. First an extremely careful fusion, conducted at a low temperature, during which, by the direct action of the air, nearly the whole of the deleterious matters and a large portion of the copper are oxidised; and secondly, a fusion conducted at a very high temperature, during which, after having scorified the oxides formed by means of the silica present, the matt not decomposed by the copper contained in the slags react on the sulphide of iron present in the matt. Blue metal is the only source of copper employed in this operation, but it is important to be remarked that its surface is thickly coated with siliceous sand, furnished by the moulds in which it has been cast, and which plays a very important part in the metallurgic changes which take place during its subsequent treatment.

No reagents are employed except the siliceous matters of the furnace, and the oxygen furnished by the admission of atmospheric air. The air introduced during the first division of the process, determines the production of the metallic oxides, and the bricks, sand, and clay, of the apparatus give rise, by their combination with these oxides, to the formation of the siliceous slags so indispensable to the subsequent improvement of the matt.

The furnace in which these reactions take place closely resembles that employed for the fusion of slags in the VIth operation; it is provided with a lateral door, which, together with that at the end of the hearth farthest removed from the grate, serves for the introduction of the charge. The tap-hole is situated at the other side of the furnace, exactly opposite the lateral door, and the only particular in which it differs from the preceding, is that it has an opening, or air-hole, situated on one side of the fire-bridge, similar to that of the ordinary roasting furnace, and which in this case serves to introduce, during the first period of the operation, a large quantity of air over the surface of the matters spread on the hearth.

The charge of a furnace of this kind is two tons of blue metal, which usually remains in the furnace rather less than twelve hours. It is essential to the success of this operation that the sulphide should be added in rather large fragments, and since the blue metal is rather fragile, precautions must be taken to prevent its division into small pieces during the process of charging.

VIII.—The eighth operation, which is the last of the series constituting the extra process, comprises the two methods of purification employed in the stages VI. and VII. The furnace is in every way similar to that used for the VIIth roasting, and the working of the charge may be divided into two distinct periods. During the first, the true roasting or slow fusion of the white metal under the oxidising influence of atmospheric air is effected : and in the second stage the refining of the matt is completed by the reaction of a stratum of copper slag. The substances charged into this furnace consist of the white metal of the VIIth roasting, together with the red and white matt obtained from the VIth fusion ; but these two products are always separately treated, because the copper obtained from them differs materially in quality. The reagents by which these metallurgic transformations are produced, are the oxygen of the air, and the sand bricks and other siliceous matters of which the furnace is constructed. The duration of each operation is  $3\frac{3}{4}$  hours, and the ordinary weight of the charge introduced  $1\frac{1}{4}$  tons.

The products obtained from this process consist of a rich copper slag, a matt containing a large per-centage of copper, called regulus, and an impure kind of metallic copper, called bottoms.

IX.—The foregoing series of operations, although extremely complicated in their details, yield, with the exception of the intermediate products, but a very limited number of definite metallurgic compounds—viz., ordinary white metal obtained by the IVth fusion; the reguline matters obtained from the extra process V., or the remelting of slags VI., which are purified by the roastings VII. and VIII.; and finally, the copper bottoms produced either during the same operation, or in the fusion of the slags VI.

All these different products are united in the IXth operation, the aim of which is to expel by roasting, in the form of sulphurous acid, the sulphur which has heretofore been preserved as a means of concentrating the copper. At the same time, all impurities, such as iron, cobalt, nickel, arsenic, antimony, and tin, are sought to be eliminated either by the direct action of atmospheric air alone, or by the combined agency of the oxygen of the air and the siliceous matters present in the furnace. These objects are attained through the medium of two successive metallurgic reactions which are separately conducted in the same furnace.

The first of these operations, or the roasting of the matt, is produced by the direct action of atmospheric air on the substance, maintained for a considerable time near the point of its fusion, by which means the charge is finally made to fall drop by drop on the bottom of the furnace. During the second period, the oxide of copper, which is produced in large quantity, reacts on the sulphides which have not become decomposed during the process of roasting, which are thereby not only purified, but at the same time much enriched. The two products resulting from this operation are crude copper, and scoriæ extremely rich in that metal, and these are reserved to be added to the roasted coarse metal in a subsequent fusion for white matt. This operation is carried on in a reverberatory furnace similar to those provided with a lateral door before described, and through this the charges of matt are introduced. The matts, which have been run into cakes of considerable dimensions, are piled on the floor of the furnace, and addition is sometimes made of some rich oxidised minerals belonging to the

### ENGLISH METHOD OF COPPER-SMELTING.

fifth class. The weight of the charge varies from three to three and a half tons; and, at the expiration of about half an hour after its introduction, the matt begins to melt, and falls slowly on the bottom of the hearth. At the expiration of about four hours the fusion is completed, and the matters collected on the hearth begin to boil, from the rapid evolution of sulphurous acid produced by the reaction of the oxide of copper on the sulphides of which the matts principally consist. In order that this phenomenon may be prolonged during a considerable time, the temperature is at this stage allowed to fall very considerably, and, at the expiration of about twelve hours, the evolution of sulphurous acid will, from the low temperature of the furnace, have entirely ceased. The fire is now again increased, and the charge brought to the liquid state, by which means the action is completed by the further evolution of sulphurous acid, and, at the expiration of eighteen hours from first charging, the copper retains but a very minute proportion of combined sulphur. The smelter now increases to the utmost the heat of his furnace, so as to produce the complete separation of the different matters which it contains; and, at the expiration of twenty-four hours, after having first skimmed the surface with a rake, he taps the liquid metal into rectangular moulds formed in the floor of the building in which the furnaces are situated.

This coarse copper, when it has cooled, is covered on the surface with numerous small blisters, and the slags resulting from the operation frequently contain as much as twenty per cent. of copper.

X.—The coarse copper obtained from the above method of treatment is now subjected to a process of toughening and refining. The furnace in which this is conducted differs but little from the other fusing furnaces of the Welsh method, except that the fire-place is made deeper, to afford the facility of accumulating a larger mass of combustible; and the arch over the sole is higher, to give the necessary space for the large charges of coarse metal with which it is supplied. The coarse copper is charged on the sole of the furnace to the amount of from seven to ten tons, and without any admixture of other matter; as the only reagents employed are the oxygen of the air and the siliceous matter furnished by the sand adhering to the pigs of crude copper, and that obtained from the bricks, &c., of which the furnace itself is composed.

The cakes of copper to be refined are piled in the form of a hollow heap, which extends to the upper arch of the furnace, and care is taken to so arrange the different ingots as to allow a

sufficient space for the free circulation of air between them. The working of a charge extends over twenty-four hours, including the time necessary for the introduction of the copper. During the first eighteen hours but little attention is required, except for keeping the grate supplied with a proper quantity of fuel. The copper is in this way gradually liquefied, and at the same time partially oxidised. The oxide of copper formed reacts either immediately, or after its combination with silica, on the substances present, more readily oxidisele than itself; and by this action a slag is formed which, besides containing a large portion of oxide of copper, carries off in combination the oxides of the different associated metals.

When the furnace has been in action during twenty-two hours, the copper is entirely freed both from the sulphur and the other metals which it originally contained, and the workman clears the bath by raking off the scoriæ accumulated on its surface. The copper in this state contains a certain portion of oxygen in chemical combination, in order to eliminate which the metallic bath is subjected to the following treatment, by which its reduction is completely effected. When the charge, with the exception of the small proportion of combined oxide, is in a state of sufficient purity, two or three shovelfuls of finely-powdered coal or charcoal are thrown on the hearth, and rapidly spread over the surface of the liquid metal. This slight covering of carbon tends to the reduction of the oxide of copper formed on the surface of the metal; and after a short interval, during which the charcoal is allowed to act alone, a long pole of green wood (generally birch) is plunged into the fused copper. Under the influence of the elevated temperature to which the wood is thus suddenly exposed. large quantities of highly reducing gases are by its decomposition evolved with strong ebullition of the metal, by which the reduction of the oxide is determined with much greater rapidity than by the action of the powdered charcoal alone, but which still not only assists in the removal of the oxygen, but also prevents the absorption of a further amount when the surface of the liquid metal is in a state of rest after the removal of the pole. When the bath has by this means been kept in a boiling state during about twenty minutes, the refiner takes from the furnace a sample of the metal by inserting in the bath the end of an iron bar around which a small lump of copper is speedily formed. This thimble-shaped sample is, whilst still hot, readily removed from the end of the bar by a steel chisel, and its purity and freedom from oxide are then judged of by testing its malleability by hammering on an anvil, and its tenacity by repeatedly

bending it backwards and forwards when firmly held in the jaws of a large vice.

As soon as, from these trials and the colour of the metal, this process is thought to be sufficiently advanced, the charcoal and a small quantity of slag is rapidly removed from the surface of the bath by a rake, and the metal transported into proper moulds by large iron ladles, which are sometimes internally lined with clay. When the copper is found to be in a proper state for removal from the furnace, it is necessary that the operation should be commenced with the slightest possible delay, as it would otherwise be liable to again become brittle, either by absorbing oxygen from the air, or chemically combining with a portion of the carbon furnished by the wood and charcoal employed.

When copper is difficult to refine, a few pounds of lead are added to it immediately after removing the door to skim the surface. This metal, from the facility with which it oxidises, acts as a purifier, and assists the scorification of the iron and other impurities which may be present.

## NAPIER'S COPPER PROCESS.

In all the various processes employed for the separation of copper from its ores, it is of the greatest importance to separate, at the earliest possible stage of their treatment, the large quantities of earthy and siliceous matters with which they are invariably associated.

To do this the mineral is commonly roasted in a reverberatory furnace, either until a sufficient amount of oxide of iron has been liberated to form a fusible slag, by combining with the non-metallic impurities present in the ore; or, as this would frequently necessitate a very prolonged calcination, such a mixture of ores is operated on as may afford fusible and tolerably liquid scorize when strongly heated, after a less complete roasting than that requisite in the other cases. In this way ores rich in the earths and oxide of iron are commonly added to those in which siliceous matters predominate, and *vice versâ*; and thus, by a judicious mixture of this kind, fluid slags are produced at a much less expenditure both of time and money, than would be required for their separate treatment.

The ordinary routine followed in the Welsh copper works, although more or less modified in the different establishments, is in all cases a tedious and very expensive operation; and the object of Mr. Napier's patent process is, therefore, to obtain equally good results in much less time, and at a smaller expenditure of

fuel. The ordinary method, as we have already seen, includes ten distinct operations, whilst the improved process reduces their number to one-half.

A mixture of Cornish ores, made according to the principle before laid down, is first calcined, and subsequently mixed, after its removal from the furnace, with a proper proportion of partially calcined rich sulphides, such as those from Cuba, called Cuba and Cobre ores; care being taken that the quantities of each be so arranged as to afford a fusible slag by the fusion and combination of their different gangues.

It is also necessary that this mixing be made in such proportion that, besides producing a clean slag, it may afford a reguline matt containing above thirty and less than fifty per cent. of metal. The fusion of this mixture is conducted in an ordinary reducing furnace similar to that employed in the second operation of the old process: and after the removal of the slags from the surface of the bath, a small quantity either of soda-ash or salt cake is thrown on the fused sulphides. When salt cake is employed, which, of the two, is the better adapted for this purpose, 1 cwt. to 1<sup>1</sup>/<sub>2</sub> cwt., together with 20 or 30 lbs. of fine coal, are added to every ton weight of regulus operated on. When these substances have been thrown into the furnace, they are thoroughly mixed and stirred together by a continued rabbling with an iron paddle; and, after having been allowed to remain a sufficient time to admit of the reduction of the sulphate of soda by the action of the charcoal, which is usually completed in the course of a few minutes, the regulus is tapped into sand-beds, where it receives the form of rectangular prisms. These are allowed to remain in the moulds until they become set; but as soon as they have acquired sufficient solidity to bear removal, they are thrown into a tank of water, in which they crumble almost immediately into a fine sandy powder. This is now thoroughly washed with water, and, after being allowed to dry, is calcined until the whole of the sulphur is expelled, which, from the fine state of division of the powder, is accomplished in from twenty-four to thirty hours. The powder, which is now thoroughly calcined, or, as it is technically called, roasted dead, is mixed with a proper quantity of malachite, or any other ore of copper free from sulphur, but containing a large excess of silica; and, after having added the requisite proportion of carbonaceous matter, it is charged into a properly arranged melting furnace, and again fused. This operation occupies from six to eight hours, and, if carefully conducted, yields metallic copper, and a clean slag containing very little metal, either in the form of enclosed shot or combined oxide.

Besides possessing the advantage of being more expeditious and less expensive than the ordinary method of treatment, this process yields from any given sample of ore a purer description of copper than can be obtained by the old method, as the sulphide of sodium produced by the decomposition of the salt cake, and subsequently dissolved by the water into which the hot pigs are thrown, carries off with it in solution such impurities as tin and antimony, which are readily soluble in that menstruum. The copper obtained from this fourth operation is in the same condition, although generally more free from impurities, as that resulting from the ninth operation of the ordinary process, and undergoes a similar reduction of the combined oxide, which, in the present instance, makes the fifth process to which the ore has been subjected.

When the slags produced during the second and fourth operations are not sufficiently fluid, it has been sometimes found advantageous to add to each charge about twenty pounds of slaked lime and a few pounds of salt, which, affording bases for a certain amount of silica, give rise to the formation of polysilicates, which are much more readily fused than those compounds in which the silicic acid is combined with but a single base.

When the ores to be treated are either carbonates or oxides, containing but a small per-centage of lime, or any other base, and a large excess of silica, it is found advantageous, in addition to the ordinary sulphides necessary for the production of a matt, to fuse them with a small admixture of the black magnetic iron scale obtained from the rolling mill and forge hammer. From  $2\frac{1}{2}$  cwts. to  $3\frac{1}{2}$  cwts. of this flux to each charge will be found sufficient to effect the fusion of the most refractory kinds of ore; and although, from its greater cheapness, lime is the most common flux employed, it yields far less fusible slags than those resulting from the iron scale.

Instead of using iron scale, rich iron slags and native carbonates of iron may be employed; but hematite, and the other ores containing peroxide of iron, are objectionable, from the oxidising action which they exert on the copper, and which is not remedied by the addition of a large excess of coal.

In this, as in the ordinary process, however, the addition of direct fluxes is to be as much as possible avoided; and when the experienced smelter has the choice of a good selection of ores, fluxes will very seldom be required.

## METHOD OF RIVOT AND PHILLIPS.

This method, which was patented in France in 1846 by M.

Rivot, Professor of Chemistry at the Ecole des Mines, and M. E. Phillips, Ingénieur des Mines of the same institution, is dependent for its action on the fact, that at elevated temperatures iron has a greater affinity than copper for oxygen. Advantage is taken of this circumstance in the following way:—

The ore, if sufficiently rich—or, if not, a mixture of the ore with a portion of the matt obtained from a fusion in the ordinary way,—is first reduced to the state of fine powder, and then roasted *dead*, so as to expel the last traces of the sulphur which it contained. When this has been effected, iron bars are introduced through apertures left in the side of the hearth, and which are closed during the former part of the operation. On the introduction of these, they become rapidly attacked at the expense of the oxygen of the oxide of copper, which is thereby reduced to the metallic state, whilst the oxide of iron formed unites with the siliceous matters present, and gives rise to a fusible slag, which is extremely liquid and entirely free from any enclosed granules of metallic copper.

This process has not yet been tried on an extensive scale; but during the progress of the experiments made at Paris, in a small furnace erected for that purpose, metallic copper of good quality was frequently obtained in one operation. When, however, arsenic is present in considerable quantity in the ores treated, it is found to affect materially the quality of the metal produced, and in this respect the process is inferior to that of Napier, in which the arsenic is carried off in solution with sulphide of sodium.

The process of Rivot and Phillips has also the disadvantage of requiring the destruction of a quantity of iron nearly equivalent in weight to the copper produced, which is, in a practical point of view, a serious objection to their method.

## BANKART'S PROCESS.

A new process of treating the various sulphides has also been patented by Mr. Bankart, who carried out his inventions on an extensive scale at the Red Jacket Copper Works, near the town of Neath. The minerals operated on in this establishment are Cuban ores, furnished by the Cobre Mining Company, and are chiefly composed of copper pyrites containing from fourteen to twenty-five per cent. of metal. This is first reduced by mechanical means to the state of fine powder, and then exposed in a proper furnace to a low red heat for several hours, with a free access of atmospheric air. By this method of treatment a large proportion

## TREATMENT OF THE COPPER SCHISTS OF MANSFELD. 369

of the sulphur present is driven off in the form of sulphurous acid gas, whilst another portion is converted into sulphuric acid, which combines with the oxide of copper formed during the operation of roasting; and the sulphate of that metal, or blue vitricl, is consequently produced.

The ore is next removed into large vats, where it is immersed in boiling water, which, by filtering through it, dissolves and carries away in solution all the sulphate of copper present, and leaves the ore chiefly in the state of oxide of copper and peroxide of iron, associated with the siliceous matrix. This residue is now again roasted with a due admixture of the same mineral in the raw state; and the sulphur of the latter, which would otherwise have gone off in the state of sulphurous acid gas, receives, through the agency of the peroxide of iron in the ore, an additional atom of oxygen, by which it is converted into sulphuric acid: this again acts on a considerable portion of free oxide of copper, and uniting with it, forms sulphate of copper, to be again extracted by solution in boiling water, as before described.

These successive operations are continued until almost the whole of the copper has been extracted, and a residue has been obtained consisting exclusively of silica and peroxide of iron.

To obtain the metallic copper from these solutions, pieces of wrought or cast iron are immersed in the liquid, when, by the action of a well-known chemical affinity, the acid and oxygen desert the copper and transfer themselves to the iron with the formation of sulphate of iron, depositing at the same time the copper in a pure crystalline and metallic state, requiring merely a simple fusion to convert it into cake copper of almost chemical purity.

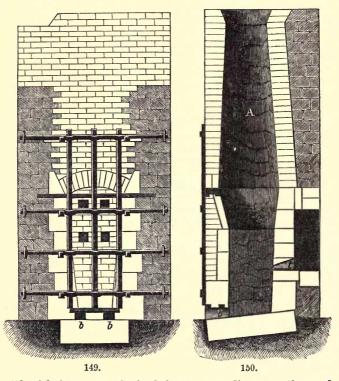
There can be no doubt but that this process is capable of producing copper of great purity. When, however, it is remembered, that to produce one ton of metal it is necessary to dissolve  $17\frac{1}{2}$ cwts. of metallic iron, and that this gives rise to the formation of no less than 4 tons 7 cwts. of copperas, it becomes evident that the test of experience will be required before this method can be pronounced superior to those already in use.

## TREATMENT OF THE COPPER SCHISTS OF MANSFELD.

On the continent of Europe, the methods of treating the ores of copper are made to differ both in accordance with the composition of the mineral operated on, and also with regard to the nature of the fuel most abundant in the locality; but a description of the routine employed for the reduction of the copper schists of Mans-

feld will afford a sufficient illustration of the continental processes. These schists, which are strongly impregnated with bituminous matter, and contain numerous disseminated crystals of iron pyrites, vary considerably with regard to their richness in copper.<sup>1</sup> The metallurgic treatment is commenced by roasting the shale in heaps interstratified with wood, by which the fire being first communicated, is afterwards carried on at the expense of the inflammable bitumen contained in the mineral itself.

To the schist, after its calcination, is added from 6 to 20 per cent. of fluor spar, together with a certain amount of slag, mode-



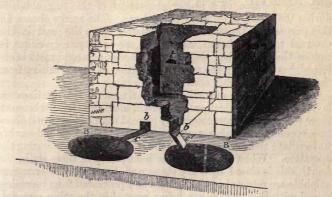
rately rich in copper, obtained from a preceding operation, and occasionally a small quantity of copper schist containing carbonate of lime. The smelting furnaces in which this mixture is reduced

<sup>1</sup> The mineral treated usually contains from 1 to 4 per cent. of copper.

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are cupolas, varying from 14 to 16 feet in height, and are supplied either with ordinary coke, or a mixture of gas-coke and charcoal. Fig. 149 represents a front elevation of this apparatus, and fig. 150 a vertical section through the axis of one of its tuyeres, t. The parts of this furnace in the neighbourhood of the tuyeres are constructed of a sort of refractory pudding-stone, whilst the upper part of the cone,  $\lambda$ , is built of fire-bricks. The air is supplied through nozzles placed either on the same side of the hearth, or on the two opposite lateral faces of the furnace, and at an equal height from



151.

the bottom of the crucible. At the lowest part of the breast of the hearth are two apertures, b, fig. 151, which are alternately opened, in order to run out the liquid products.

These openings communicate, by means of the channels, cc', with the external basins, B, B', three feet in diameter, and twenty inches in depth. The combustible and mineral are charged in regular consecutive strata, and a slag nozzle, of from six to seven inches in length, is allowed to form beyond the extremity of the tuyeres. These cupolas are surmounted by chimnies from thirty-five to fifty feet in height, by which the smoke and vapours are carried high into the atmosphere. The matts and slags flow constantly out of the furnace, and are received in one of the external basins prepared for that purpose. When one of these has become full, the aperture by which it communicates with the furnace is closed, whilst that connected with the other is opened : so that the liquid matters flowing from the furnace are alternately conducted into each of these basins. At Mansfeld the fused scorize are usually moulded in the form of large bricks, and are extensively employed in the construction of houses in the vicinity of the works. The matts

are removed from the basin in the form of circular plates, which are lifted off, when sufficiently cool, from the surface of the still liquid sulphides remaining in the bottom of the cavity.

The matt thus obtained seldom amounts to more than 1-10th of the weight of the mineral operated on, and consists of a mixture of the sulphides of iron and copper, containing from 20 to 60 per cent. of the latter metal. When it contains from 20 to 30 per cent. of copper, it is subjected to three successive roastings on layers of wood, and afterwards again passed through the furnace with the addition of a proper proportion of the slag obtained during the fusion of ordinary roasted ore. The scorize chosen for this purpose are those which immediately cover the matt in the external receiving basins, and which are consequently richer in copper than the other slags. In this way a second matt is obtained, having nearly the same composition as that resulting from the fusion of the richer ores.

These rich matts are subjected to six successive roastings on lavers of dry wood, which are executed in small areas formed between three walls. These are commonly pierced with sundry small channels, opening at their lower extremity towards the heap, and serving to facilitate the escape of the smoke and gases given off during the operation. When the matts have been placed in these stalls, the fourth side is closed by a dry stone wall, by which the lumps of sulphide are retained in their places and prevented from becoming mixed with those which are being roasted in the other compartments of the area. When the matt has undergone the process of calcination in the first stall, it is transferred to the second, and so on in succession until it has arrived in the sixth and last division. where the operation is completed. During these successive roastings a considerable quantity of sulphate of copper is formed through the oxidation of the sulphides of which the matt is composed; and this, after being removed by lixiviation, is obtained in a crystalline form by the evaporation of the liquors. All the matts after their calcination are, between each separate roasting, exposed to the action of water in large wooden troughs, so arranged on the side of a hill as to allow of the contents of one being run through a proper spout immediately into another placed beneath By this methodical system of washing, the liquors are at it. length obtained in a tolerably concentrated state, and consequently afford crystals of sulphate of copper after a moderate degree of concentration in large leaden pans, heated from beneath by a slow fire.

The roasted matt is melted in a cupola furnace similar to that in which the fusion of the mineral itself is effected, but of smaller dimensions. The charge consists of a mixture of the calcined matt

## TREATMENT OF THE COPPER SCHISTS OF MANSFELD. 373

and a due proportion of slags from the first operation, which are added with a view to the removal of the oxide of iron originally present in the fused sulphides. This fusion gives rise to the formation of three distinct products—viz., black copper, a reguline matt, and slags of various degrees of richness. The black copper is removed from the exterior basin in the form of discs, obtained by throwing water on the liquid metal and the subsequent removal by an iron bar of the circular cake thus solidified. The black copper obtained contains about 95 per cent. of copper, from 3 to 4 per cent of iron, and 1 per cent. of sulphur, together with small quantities of antimony and silver.

The matt is extremely rich in copper, and is added to the richest of the second matts obtained from a former operation.

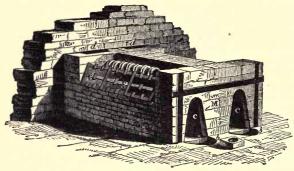
It sometimes happens that these ores contain a sufficient amount of silver to render its extraction a matter of importance; and in this case the separation may be made either from the last matt after it has been roasted, or from the black copper before it has been subjected to the process of refining.

The silver is obtained from the black copper by a process called *liquation*, and from the roasted matts by an *amalgamation* with mercury. The efficiency of the process of liquation depends on the following principles :—If lead and copper be fused together, the two metals will be found to unite and form an alloy; and if this mixture be suddenly or rapidly cooled after being run out of the furnace, they remain in a state of intimate admixture. If, however, on the contrary, the alloy be slowly heated to near its point of fusion, or be allowed to cool very gradually after being in a liquid state, the two metals are found to separate, and the lead will contain nearly the whole of the silver which originally existed in combination only a small portion of the lead added. The silver may now be separated from the lead by cupellation, and the copper freed from the adhering lead by an operation called refining.

In practice, three parts of black copper and from ten to twelve parts of lead, already containing a certain portion of silver—if such is to be procured—are fused together in a cupola furnace: instead of metallic lead, litharge rich in silver is sometimes employed. The fused alloy, on flowing from the furnace, is received in cast iron moulds, where it is rapidly cooled by the help of water, and from which it is removed in the form of large circular cakes. These discs are subsequently heated on a liquation hearth, in order to extract the argentiferous lead in the liquid form, whilst the associated copper remains unmelted and forms a porous mass, retaining very nearly the same form as the original cakes of alloy.

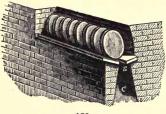
This hearth, figs. 152 and 153, consists of two slightly inclined

plates of cast iron, so placed as to leave between them a small space, s, beneath which is a hollow channel, c, left in the mass of masonry, M, which supports the iron plates. The discs of alloy are placed perpendicularly on these, and are kept at a short distance from each other by means of wooden wedges, whilst the open sides of the



152.

area are closed, after charging the alloy, by thick plates of sheet iron, F. The fuel employed, which is wood charcoal, is introduced between the metallic discs after which the wooden wedges



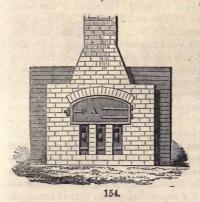
153.

are withdrawn, and some wood is placed in the channels, c, by the combustion of which the charcoal in the upper part of the hearth is readily ignited: the draught is produced by the small chimnies, d, left in the masonry of the furnace. As the temperature of the cakes becomes more and more elevated, the lead, which

is the most fusible metal present, begins to melt, and, 'Howing on the surface of the iron plates, falls into the channels, c, and is conducted, by a slight depression in the floor, into the exterior basins, b. In proportion as these reservoirs become filled, the lead is removed with an iron ladle to a mould, where it receives the form of small lenticular cakes. The copper, still retaining a certain amount of lead and silver, remains, in the form of half-fused spongy masses, in the position in which it was first placed. The lead thus separated by liquation contains almost the whole of the silver, as, from the circumstance of the alloy of silver and lead being more fusible than the pure metal, a very small quantity only of silver is retained by the lead which remains associated with the spongy copper on the area of the furnace.

These porous masses of copper are, however, still capable of affording a certain amount of argentiferous lead, if submitted to a higher temperature, and for this purpose they are heated in a peculiarly constructed apparatus, known by the name of a sweating furnace.

Fig. 154 represents an elevation of this furnace, and fig. 155 a horizontal section, made at the level of the bottom of the door, A.





155.

The spongy masses of copper remaining after the liquation of the lead and silver, are charged on the sole of the furnace, above the top of the flues, F, and resting on the brick piers by which they are divided from each other. The spaces, F, are now filled with wood, which is ignited, and the door, A, is closed. The draught is established through the openings, f, in connection with a chimney, by which the smoke and heated air are carried off.

This treatment determines the separation, in a liquid form, of a further portion of lead, but as the air passing through the furnace is possessed of highly oxidising properties, the larger proportion is converted into litharge, which falls to the bottom of

the spaces, F, together with a small quantity of oxide of copper dissolved in the more fusible oxide of lead. By operating in this way we obtain on the sole black copper, still further freed from lead and silver than that coming from the liquation hearth, and in the spaces, F, will be accumulated a litharge rich in silver, and containing a small proportion of oxide of copper.

This last mixture is employed as a source of lead in the cupolas in which the fusion of the black copper with lead is conducted.

The black copper obtained from the Mansfeld process is refined in a reverberatory furnace closely resembling the German cupelling furnace to be hereafter described.

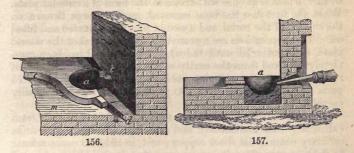
The fuel employed is wood, which is consumed on a grate, from whence the heated air diffuses itself in the body of the furnace, and then passes off by the chimney. The copper to be purified is piled on the sole, which is composed of a mixture of charcoaldust and clay firmly consolidated with a rammer. The black copper is charged through a door, which is closed immediately after its introduction; and as soon as the metal is melted, a current of air is made to play constantly on its surface from two tuyeres, the nozzles of which are furnished with butterflies, or loose pendant valves, for the purpose of spreading the effect of the blast equally over the whole surface of the metallic bath. When exposed to these oxidising influences, the sulphur, iron, and lead are first acted on, and give rise to the formation of slags, which are raked through the door. At the expiration of a certain time the copper becomes free from all other metals with which it was associated, and its surface is covered with a slag of a red colour, extremely rich in protoxide of copper. As the process advances, the workman extracts samples of copper at frequent intervals, by introducing into the furnace an iron bar, around the end of which a sort of metallic thimble is quickly formed, and this, on being hammered, affords the means of ascertaining the precise point at which the operation should be terminated. When the metal has been sufficiently refined, the charge is at once run out into two external basins, where a little water is thrown on its surface, in order to determine the solidification of a superficial crust: this is removed by a hooked bar of iron in the form of a thin circular plate. More water is now thrown on the fused mass, and other discs are successively obtained, until the whole of the charge has been removed from the external reservoirs. These plates, which are called rosettes, are of a fine red colour, and covered on the surface with numerous blisters similar to those observed on ordinary cemented steel: they also retain a small proportion of the red oxide by which their ductility and malleability are considerably impaired.

This purification of black copper is sometimes accomplished previous to the addition of the lead necessary for the purposes of liquation; but, in other cases, the operation is not carried to the same extent, and the partially refined metal is finely granulated by being run out of the furnace into a large cistern of water. These granules are subsequently melted in a cupola, with the addition of either litharge or metallic lead, by which a more homogeneous alloy is obtained than by the direct fusion of the black copper with lead. This mixture is moulded into discs in the usual way, and after the process of liquation and sweating, the remaining cupreous matters are refined, and toughened in a small blast hearth, called in German *Kupfergahrheerd*.

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When the black copper does not contain a sufficient amount of silver to pay for its extraction, it is not subjected to the process of liquation, but is at once refined in the small German hearth.

Fig. 156 represents a perspective view; and fig. 157 a vertical section of this arrangement, which consists of a hemispheric basin, a, about 16 inches in diameter, interiorly lined with a composi-



tion formed of one part of pounded charcoal, and two parts of fireclay. This is surrounded by a low iron curb, c, which is intended to keep the fuel from being scattered, and is furnished with a small iron door, d. When the crucible has been fresh lined, it is necessary, before proceeding with another operation, to dry it by the introduction of a few shovelfuls of ignited charcoal, which is allowed to remain until the hearth is completely dried. As soon as this is the case, the cavity is filled with fresh charcoal, fragments of black copper are arranged opposite the tuyere, t, and the blast is gradually admitted. When the first charge of crude metal has been thus melted a further quantity is added, care being taken at the same time to supply the hearth with a proper amount of fuel. The scoriæ formed during the progress of the operation escape through a tap-hole, which communicates with the cavity in which the refining is effected, a little below the level of the top of the mass of masonry, m.

The first slags obtained are of a greenish colour, and contain a large quantity of oxide of iron; during the fusion, sulphurous acid, and sometimes white antimonial vapours, are evolved.

The next slags are of a deep red colour, and are extremely rich in dinoxide of copper. When the whole of the black copper constituting a charge has been fused in successive small quantities, the workman takes samples from time to time by means of an iron rod, and, from the appearance of these, he is enabled to judge of the working of the furnace, and the state of the metal it contains. As soon as the process is found to be sufficiently

#### COPPER.

advanced, the blast is suddenly stopped, and a pailful of water thrown on the surface of the metal, which is immediately afterwards freed from the fragments of charcoal by which it is surrounded.

The scoriæ are then carefully raked off from the surface of the bath, on which a little water is again thrown to solidify the upper surface, which is at once withdrawn in the form of a circular plate. When the first disc has been removed, more water is thrown on the surface of the metal, and a second film is coagulated and lifted off. These operations are repeated after the removal of the second plate, and continued until the whole of the metal has been completely removed from the cavity of the furnace. The process of refining commonly occupies about two hours, and affords 75 parts of rosette copper from 100 parts of black copper originally operated on.

The rosettes obtained by these methods of refining are far from exhibiting that malleability and ductility which we observe in ordinary commercial sheet copper ; and, in order to communicate to it these properties, it is necessary that it should be subjected to a final and very delicate operation, which can only be successfully conducted by workmen of considerable experience. This toughening is not on the Continent effected in the establishments where the rosette copper itself is produced, but is more commonly performed in the workshop of the copper-smith, by whom the softened metal is converted into the various utensils for which it is employed.

For this purpose the rosettes are again melted in a little furnace, similar to that above represented; and as soon as the discs are fused, and have fallen into the small concave basin, the surface of the bath is sparingly covered with small pieces of charcoal, by which, after a certain time, the oxide is entirely reduced, and the metal attains its state of greatest malleability. If, however, the exact moment for stopping the operation is not seized—*i.e.* when all oxide has been completely reduced, it again gradually loses its ductility, from entering into combination with a portion of the carbon by the aid of which the oxide was at first reduced.

When this occurs, which is easily ascertained by the refiner, who constantly takes samples by the aid of an iron rod, he removes the fuel from the metal, and allows the blast from the tuyere to play during a few minutes directly on the surface of the bath. These operations are repeated until the right *pitch* has been seized, when the metal is either run off into ingots, or is cast into any form which it may be required to assume. The great art in this method of refining is to hit as soon as possible the exact point at which the operation should terminate, since, if these reactions be unnecessarily prolonged, the various losses incident on the purification of the copper will be considerably increased.

The method employed for the separation of silver by amalgamation from copper matts containing that metal, will be described when treating of the metallurgical treatment of the various ores of silver; but when lead ores and fuel are to be obtained with tolerable facility, and at a moderate cost, the separation is in most instances more advantageously conducted by a proper system of liquation.

The process above described is capable of producing copper of great chemical purity; but in this respect it never surpasses the "selected refined" metal of our own smelters.

Brass and other Alloys of Copper.—Pure copper is but little adapted for moulding, as it not only requires a considerable degree of heat to effect its fusion, but is also extremely liable to yield imperfect and air-blown castings. These inconveniences are obviated by the addition of some other metal, such as tin or zinc.

With the addition of a proper quantity of the latter, an alloy is produced, which not only fuses readily and affords good castings, but which is also more easily worked than pure copper either at the vice or in the lathe. The addition of zinc materially affects the colour of the copper with which it is combined. When added in small proportion only, the alloy assumes a golden-yellow colour; if the per-centage of zinc be more considerable, a pale-straw colour is obtained, and if the zinc predominates, the colour of the alloy is grevish-white, or iron-grey.

Various alloys of this kind are employed in the arts, of which the most important is known by the name of *brass*. The proportions of the two metals best calculated for the production of fine brass seems to be two equivalents, or 63.5 parts of copper, and 32.2 parts or one equivalent of zinc, or very nearly two parts by weight of the former to one of the latter. The bright coloured alloy known as Prince Rupert's metal, consists of one equivalent of zinc and one of copper, or nearly equal weights of each.

Brass or hard solder consists of two parts of brass and one of zinc, to which a little tin is occasionally added; but when the solder is required to be very strong, as for uniting the edges of tubes intended to subsequently undergo drawing, two parts of common brass, and two-thirds of a part of zinc, are employed. Mosaic gold consists of 65 parts of copper, and 35 of zinc. Bath metal is composed of 78 parts of copper and 22 of zinc. Pinchbeck and Mannheim gold are merely different names for an alloy similar to Prince's metal, and which is composed of three parts of copper and one of zinc, separately melted in different erucibles, and afterwards suddenly mixed and incorporated by stirring. The

#### COPPER.

preparation of brass may be variously conducted. In some localities the copper and zinc are directly melted together, as at the manufactory of Hegermühl, on the Finon Canal near Potsdam, where 44 lbs. of old brass, 53 lbs. of refined copper granulated, and 24 lbs. of zinc are operated on at one time. The mixture, which weighs 120 lbs., is divided into four crucibles, and melted in a wind furnace with pit coal fuel. The loss experienced during the fusion of a charge of this kind varies from two and a-half to four pounds. Instead of operating in this way, slips of copper are sometimes plunged into melted zinc until a somewhat infusible alloy is obtained, when the heat is raised, and the remainder of the copper added.

The brass thus obtained is broken into small pieces, and again melted with a fresh quantity of zinc to obtain the finished alloy. When the mixed metal is intended to be rolled into sheets, it is first cast into thin plates by pouring it in a mould, the sides of which are made of two flat slabs of granite, mounted in an iron frame, and kept at the requisite distance from each other by parallel bars of the same metal. After having once or twice passed through the rolling-mill the plates become too hard to laminate with facility, and are annealed by being heated to redness, and allowed to cool slowly before they are again passed between the rollers. This process is repeated as often as the sheets become too hard to be conveniently wrought, and when considerably reduced in thickness, two or three, or even six or seven sheets, are passed together between the rollers. When only small quantities of brass are required, it is made by melting in an earthen or black-lead crucible a mixture of copper and old brass, to which, immediately before the alloy is to be poured into the mould prepared for its reception, is added a proper amount of zinc. The reason for adding the zinc at so late a period of the operation is to prevent its being again driven off by the great heat to which it is exposed.

Pieces of copper are sometimes externally converted into brass by exposure when at a red heat to the vapour of zinc: in this way are prepared the copper bars from which the so-called gold wire of Lyons is manufactured.

Copper is also extensively alloyed with tin, in combination with which it yields many valuable compounds, variously named in accordance with their respective compositions and uses.

Gun-metal of which cannons are made consists of, copper 91; tin 9.

Bell-metal is composed of, copper 78; tin 22.

The alloy of which gongs and cymbals are manufactured has usually the following composition :---Copper 80; tin 20. An alloy for telescope mirrors consists of 67 parts of copper and 33 of tin, whilst that employed for medals is composed of 95 parts of copper and 5 of tin, to which a trace of zinc is occasionally added for the purpose of improving the tint.

The alloys of copper and tin, although extensively important in the present day, were evidently much more so before the use of iron was generally known, since prior to that period they were almost exclusively employed in the manufacture of cutting instruments; for this purpose a mixture of 90 parts of copper to 10 of tin was most commonly used, although a little lead was occasionally added apparently with a view of imparting to the alloy a certain degree of toughness.

The preparation and fusion of these different mixtures is, according to the quantities required, conducted either in a reverberatory furnace, or in crucibles heated by a strong coke fire.

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## COBALT.

# Equiv. = 29.52. Density = 8.53.

COBALT is a metal of a steel-grey colour, and is susceptible of receiving a high polish; but, from the difficulty experienced in its preparation, and its peculiar properties, it is never employed in the metallic state. Pure metallic cobalt may be obtained by the reduction of its oxides by the aid of heat and hydrogen gas, but the metal thus procured is, from its finely divided state, highly pyrophoric. To obtain this metal in a more compact and less oxidisable form, the oxide may be strongly heated in a porcelain tube, passing through the cavity of a large assay furnace. The reduction must in this case also be effected by a current of hydrogen gas; but from the elevated temperature at which the operation is conducted a sort of aggregation of the particles is obtained, and by this its tendency to rapid oxidation is prevented. The oxides of cobalt, like those of iron, are readily reduced by the action of carbon at an elevated temperature, and give rise to the production of a carburet of cobalt corresponding to the well-known carburet of the former metal. Cobalt is less readily than iron acted on by a moist atmosphere, but by continued exposure becomes covered by an oxide of a dark-brown colour.

#### ORES OF COBALT.

The ores of cobalt are readily distinguished from other minerals by their property of affording a fine blue colour when fused with borax before the blowpipe. The principal ores of this metal are the following :—

**Smaltine** occurs in octahedrons, cubes, and dodecahedrons, more or less modified. Colour, tin-white, inclining to steel-grey; structure, granular and uneven; density, 6.4 to 7.2. This ore essentially consists of cobalt and arsenic, although their relative proportions are subject to considerable variation. It is found in veins associated with silver and copper; occurs in Cornwall, Bohemia, Hessia, and more abundantly at Schneeberg in Saxony.

Black Oxide of Cobalt is an earthy mineral of a blue-black colour,

which occurs, more or less mixed with black oxide of manganese, in many localities, particularly in Cornwall, Germany, and Austria. It is also found in considerable abundance in the Missouri districts, United States of America. The ore from this locality analysed by Prof. Silliman, afforded 40 per cent. of oxide of cobalt associated with the oxides of nickel, manganese, iron, and copper.

Arseniate of Cobalt presents itself in thin oblique crystals, having a perfectly-defined cleavage and foliaceous structure. It also occurs as an incrustation on other minerals, and in compact reniform masses. Its colour is a pinkish-purple, resembling that of the peach-blossom; when scratched, it affords a greenish streak. This mineral is generally associated with lead and silver, or with other ores of cobalt, and is abundantly found at Schneeberg in Saxony, Saalfield in Thuringia, and Riegelsdorf in Hessia. It is also found in England, in the counties of Cornwall and Cumberland, but does not occur in this country in sufficient abundance to render its extraction a matter of commercial importance. Its composition, according to Dana, is 39.2 of oxide of cobalt, 37.9 of arsenic acid, and 22.9 of water. When heated it gives off arsenical fumes, and fused with borax, affords a bead of a fine blue colour.

The various preparations of cobalt are chiefly used for painting on pottery, and are for this purpose largely imported from Germany, either in the state of oxide or in the form of a silicate known as *smalt* or *azure blue*.

Estimation of Cobalt.—This metal is commonly estimated in the metallic state, and for this purpose the oxide obtained by precipitation with caustic potash is reduced by a current of hydrogen gas passed over it, when heated to redness, in a tube of hard German glass.

Cobalt is separated from the alkalies and alkaline earths by sulphide of ammonium, which precipitates it as sulphide. When magnesia is present in the compound examined, its precipitation must be prevented by the addition of chloride of ammonium to the solution, previous to the introduction of the alkaline sulphide. Oxide of cobalt is readily separated from alumina by excess of caustic potash, which dissolves the latter, and leaves the oxide of cobalt unaffected.

The separation of cobalt from iron is obtained in various ways, but among the most simple of these is the following :—The iron is first peroxidised by the addition of nitric acid, and after having added a sufficient amount of chloride of ammonium to keep the cobalt in solution, the iron is thrown down by an excess of ammonia. The cobalt is subsequently precipitated from the filtrate by the addition of sulphide of ammonium. The separation of copper and lead from ores of cobalt is easily obtained by sulphuretted hydrogen, which precipitates the two former without affecting the latter.

The complete separation of cobalt from manganese is attended with considerable difficulty. One of the best methods of conducting this operation is the following :—The mixed oxides are first heated in a current of hydrochloric acid gas, for the purpose of converting them into chlorides; they are then heated in the same tube, through which a current of hydrogen gas is now conducted : this reduces the chloride of cobalt to the metallic state, whilst the chloride of manganese remains unaffected, and, on treating the mixture with warm water, is completely removed in solution.

### SMALT OR AZURE BLUE.

This substance, which is extensively employed as a pigment for producing a blue colour on various kinds of pottery, as also by paper-stainers and house-painters, is chiefly manufactured in Saxony and Bohemia, where the greater portion is produced by the treatment of the natural arseniosulphide of cobalt. The ore destined for the manufacture of smalt is first roasted in a reverberatory furnace, having in communication with its flue a large chamber for the purpose of condensing the arsenical fumes which are evolved. After having been suitably roasted in this furnace, the ore is mixed with pure siliceous sand and carbonate of potash, in the proportion of 50 parts of silicic acid, 20 to 22 of alkali, and from 25 to 30 parts of the prepared mineral. The fusion is now conducted in large earthen pots, arranged in a furnace similar to those employed in the preparation of glass. The fusion of the mixture first commences at the surface, where it becomes pasty and cavernous from the gases evolved during the process. At the expiration of five hours from the charging of the furnace, the contents of the pots receive a first stirring with a long iron rod, and this is repeated once every hour until the glass has become perfectly fused and adheres firmly to the stirrer without any appearance of air bubbles. The contents of each pot are now found to be arranged in three distinct strata. The first consists of a light blue glass, which is at once removed ; the second is the true cobalt blue; and the third, which accumulates at the bottom of the pots, a fusible matt, generally containing nickel, and known by the name of Speiss. After the removal of the light blue glass, the smalt is laded out from the pots with a large iron ladle and thrown into a reservoir, through which a current of water is constantly made to flow. By this treatment it becomes split into innumerable fragments, and its subsequent pulverisation is consequently much facilitated. When the pots have been nearly emptied, the speiss

together with a little smalt, is removed by the ladle: the former being completely liquid, readily separates from the more viscous glass which adheres to the ladle, whilst the metallic matt is run into cast iron moulds. These, during the time they remain hot, give off dense arsenical vapours, and are, therefore, so placed in niches in the furnace as to be in direct communication with the draught of the chimney.

The deeply-coloured blue glass, after being removed from the vat into which it has been thrown, is first pounded under a stamping mill, and then ground with water to the state of an impalpable pulp between large granite mill-stones. The blue pulp thus obtained is afterwards suspended in water for the purpose of separating the coarser fragments, which are the first deposited, and again made to pass through the granite mills. After having been allowed to stand a certain time, the supernatant liquor is drawn off into a series of reservoirs, in which the powder gradually deposited is classified in accordance with its order of deposition. The different products thus obtained vary in colour with the greater or less fineness of the particles of which they are composed.

**Cobalt Blue, or Thenard's Blue**, is prepared by precipitating a solution of sulphate or nitrate of cobalt by phosphate of potash, and adding to the resulting gelatinous deposit from three to four times its volume of freshly deposited alumina, obtained by the addition of carbonate of soda to a solution of common alum. This mixture, after being well dried and calcined in a crucible, affords, when properly ground, a beautiful blue pigment.

# NICKEL.

# Equiv. = 29.57. Density = 8.3.

NICKEL is a metal of a greyish-white colour, much more ductile and malleable than cobalt, and possessed of magnetic properties but little inferior to those of iron, although when strongly heated this property almost entirely disappears. The surface of polished nickel is but slightly affected by exposure to a moist atmosphere, but when heated in contact with air it quickly becomes covered by a green oxide.

Pure metallic nickel may be prepared from its oxide by the process made use of in the preparation of cobalt, and when thus obtained has much the appearance of the pulverulent cobalt similarly produced. When oxide of nickel is strongly heated with charcoal, in a wind furnace, it becomes reduced to the metallic state, and, by combining with a portion of the carbon present, gives rise to the formation of a fusible carburet, which collects in the form of a button at the bottom of the crucible in which the fusion has been conducted. When treated either by hydrochloric or weak sulphuric acid, this metal dissolves with the evolution of hydrogen gas.

Ores of Nickel.—The ores of nickel, with but few exceptions, have a pale colour, and metallic lustre. In some respects they resemble those of cobalt, but are distinguished from them by not communicating a blue colour to borax, when fused before the blowpipe. Specimens of native nickel have been obtained from Westerwald, in the Erzgebirge, but it is not found in sufficient quantities to constitute an article of commerce.

**Copper Nickel**; *Kupfernickel.*—This is a mineral of a pale copper colour, affording a brownish-red streak. It usually occurs massive, and has a metallic lustre. It is extremely brittle, and has a specific gravity varying from 7.3 to 7.5. This ore is essentially composed of 44 parts of nickel and 54 of arsenic, but a portion of the latter body is not unfrequently replaced by a corresponding amount of antimony. When heated before the blowpipe, it gives off alliaceous fumes, and subsequently fuses into a pale green

globule, which darkens on exposure to the oxidising flame. Copper nickel is generally found associated with the ores of copper, silver, and cobalt, and is principally obtained from the mines of Saxony : small quantities have, however, been raised in this country, and particularly at Pengelley mine, in Cornwall.

Among the other ores belonging to this class, although, from their scarcity, of much less commercial importance than the above, may be mentioned the following :—*Nickel glance*, an arsenical ore, occurring both massive and in cubical crystals. This mineral, which is of a steel-grey colour, is found in Sweden, the Hartz, and at Schladming in Austria. It contains 38 per cent. of nickel, and has a specific gravity of about 6.7. White nickel, another arsenical ore, found at Reichelsdorf in Hesse Cassel, and Schneeberg in Saxony; it contains from 20 to 30 per cent. of nickel. *Nickel stibine*, an antimonial sulphide of nickel, containing from 25 to 29 per cent. of the latter metal. Antimonial nickel, containing 29 per cent. of nickel, and no sulphur. It is a pale copper-coloured mineral from the Andreasberg mountains.

Nickel Pyrites is a brass-yellow sulphide of nickel, occurring in rhombohedral crystals, and in delicate capillary forms. This ore, which is found in small quantities in Bohemia, Saxony, and Cornwall, contains 64 per cent. of nickel, and has a density of 5'3. *Nickeliferous pyrites*, a double sulphide of iron and nickel, of a bronze-yellow colour, containing from 2 to 22 per cent. of that metal, is obtained from southern Norway. A similar compound, containing from 10 to 12 per cent. of nickel, has recently been discovered in the neighbourhood of Inverary, in Scotland, and is noticed by Mr. King as occurring in the La Motte mine, in the U. S. of America. Another sulphide of nickel, containing bismuth, has been found in some of the Prussian mines, which have also produced specimens of arseniate of nickel of a beautiful applegreen colour.

Green Oxide of Nickel usually occurs as an incrustation on other minerals. It is nearly transparent, of a bright emerald-green colour, and has a vitreous lustre. Another oxide of nickel, of a brown, or nearly black colour, and containing variable quantities of sulphur, is found in connection with the ores of cobalt, at the mine of La Motte, in the Missouri district.

Estimation of Nickel, and its separation from Cobalt.—Nickel, like cobalt, is weighed in the metallic state, for which purpose its oxide, precipitated by caustic potash, is reduced by being heated to redness in a hard glass tube, through which a current of hydrogen gas is made to pass. The separation of nickel from other metals is effected by the same processes as are employed for the elimination of cobalt, and it will therefore be merely necessary to describe the method of separating these metals from each other. One of the most simple means by which this object may be effected is the following: To the solution containing the two oxides to be separated, is added a slight excess of oxalic acid, by which they are both precipitated. The deposit thus obtained is now redissolved in ammonia, and the solution placed in an uncorked flask, and thus left exposed to the air. By this means the ammonia is gradually dissipated, and in proportion as it is evolved the liquor loses its power of dissolving the oxalates which it contains. The two salts are not, however, equally soluble in the volatile alkali, and a point is therefore arrived at when the oxalate of nickel, which is of the two the least soluble, begins to be precipitated, whilst the whole of the oxalate of cobalt is still retained in solution. In proportion as the oxalate of nickel is deposited, the liquor gradually assumes a redder tint, and when it has acquired a full red colour, the whole of the nickel has been deposited, and the liquor containing the cobalt must be carefully syphoned off, and the precipitate washed with distilled water. The oxalate of nickel thus obtained invariably contains a small quantity of oxalate of cobalt, which must be separated by a second solution in ammonia, and exposing the liquor to spontaneous evaporation in a warm part of the laboratory.

Another method by which this separation may be effected with considerable accuracy is the following: the two oxides are first dissolved in hydrochloric acid, and the liquor afterwards considerably diluted with distilled water. The liquor is now saturated with chlorine gas, and an excess of precipitated carbonate of baryta added. The liquor, which must be cold at the time this addition is made, is afterwards set aside for about 18 hours, at the expiration of which time the cobalt will be entirely precipitated in the form of sesquioxide, whilst the nickel is retained The precipitate, consisting of sesquioxide of cobalt, in solution. and the excess of carbonate of baryta, is collected on a filter, and after being carefully washed is dissolved in hydrochloric acid. From this liquor the baryta is separated by sulphuric acid, and the sesquioxide of cobalt subsequently precipitated by caustic potash.

### METALLURGY OF NICKEL.

The nickel of commerce is chiefly obtained from kupfernickel, nickeliferous pyrites, and from the speiss obtained as a secondary product in the treatment of nickeliferous ores of cobalt. The most productive mines of this metal are those of Saxony, Germany, and Norway. The preparation of pure nickel from speiss is conducted

in accordance with a method first proposed by Wöhler. The powdered speiss is roasted, first alone, and afterwards with the addition of powdered charcoal, to effect the separation of its arsenic. The residue obtained by this process is now mixed with three parts of sulphur and one part of carbonate of potash, and then fused in a large earthen crucible. This product is now edulcorated with warm water, by which the arsenic and sulphur associated with potassium are dissolved, while the nickel, in the form of sulphide, remains at the bottom of the vessel in which the operation has been conducted. When, as sometimes happens, from the employment of too high a temperature at the commencement of the roasting, the whole of its arsenic has not been expelled, the operation must be repeated on the residual sulphide thus obtained. As soon as they have been entirely freed from arsenic, the sulphides are well washed with warm water, and then dissolved in sulphuric acid, to which a small quantity of nitric acid has been added: the precipitation of the lead, copper, and bismuth which may be present, is determined by a current of sulphuretted hydrogen gas, and the metals which still remain in solution are afterwards precipitated by an alkaline carbonate. This precipitate, after being well washed, is now treated with an excess of oxalic acid, which forms a soluble oxalate of iron, and leaves behind an insoluble oxalate of the oxides of cobalt and nickel. This residue is then dissolved in ammonia, and treated as already described. The oxalate of nickel deposited from this solution is, after being carefully washed to remove any traces of the ammoniacal liquor, ignited in a close crucible, having an aperture in the lid for the escape of the evolved gases.

It is understood that great improvements in this process have recently been made, but as the manipulations employed are kept a secret by the manufacturers, it would be difficult to ascertain the exact routine of their operations. It is, however, extremely probable that something like the following process is that now employed. The roasted ore, or speiss, after being dissolved either in sulphuric or hydrochloric acid, to which either nitric acid or nitrate of soda has been added, to peroxidise the metals, is placed in large vessels, in which the insoluble matters are allowed to subside. The clear liquor, after it has cooled, and the copper and lead have been precipitated by sulphuretted hydrogen, may be decanted off, and treated by carbonate of lime, in the form of common chalk, by which the iron, and traces of cobalt, will be precipitated, whilst the greater portion of the cobalt, and the whole of the nickel, will remain in solution. After the oxide of iron thus precipitated has subsided, and the liquor has been again syphoned off, the cobalt may be thrown down by saturating

#### NICKEL.

the solution with chlorine gas, by the addition of hypochlorite of lime, and then adding carbonate of lime or carbonate of baryta. The liquor syphoned from this solution contains the whole of the nickel, which may now be precipitated by ebullition with hydrate of lime, and dried and reduced in the usual manner.

Applications of Nickel.—The nickel obtained in this country is chiefly employed for the manufacture of Argentane, or German silver, which is an alloy of this metal with zinc and copper: nickel likewise forms one of the constituents of the tutenague of China, and the packfong of the East Indies. Being exclusively used as an alloy, the nickel of commerce comes into the market in the form of finely divided grains, or granulations of the size of small beans. The best German silver consists of 8 parts of copper, 3 of nickel, and  $3\frac{1}{2}$  parts of zinc, but a more common and inferior variety is sometimes manufactured from 8 parts of copper, 2 of nickel, and 4 of zinc.

# TIN.

# Equiv. = 58.82. Density = 7.29.

TIN is a white metal, possessed of a lustre closely approaching that of silver; it has a characteristic taste, and an odour which becomes peculiarly evident after a bar of this metal has been slightly warmed by being held for some time in the hand. It is extremely malleable, and may consequently be reduced into very thin leaves by hammering : at the temperature of 212° Fahr. this property is considerably increased.

This metal, although flexible, is not very tenacious, and when bent emits a peculiar crackling sound, called the "creaking" of tin. This phenomenon is produced by the rubbing together of the surfaces of the minute metallic crystals of which the ingot is composed, and which, by their friction against each other, cause a perceptible elevation of temperature when a bar has been repeatedly bent and again straightened.

Tin melts at a temperature of 442° Fahr. and when very strongly heated gives off distinct white fumes, which, however, appear to possess an extremely feeble tension, since a mass of metal, when heated in a smith's forge, experiences but a slight loss of weight by a prolonged exposure to a full red heat. Tin exhibits a great tendency to crystallisation, and this property may be readily made apparent by attacking its surface by some acid capable of removing the exterior pellicle. When this has been done, the surface assumes a mottled appearance, caused by the irregular reflection of the fern-like crystals brought to light by the action of the acid. A process of this kind is sometimes employed to improve the appearance of snuff-boxes, and other objects made of tin-plate, which, after being thus treated, and subsequently covered with a coating of transparent and slightly coloured varnish, present a variegated and prettily marked surface.

Tin may also be made to crystallise, by fusing a considerable weight in a ladle or crucible, which is afterwards allowed to cool very gradually in a heated sand-bath, and as soon as a solid pellicle has formed on the surface of the bath, it is pierced with a hot iron, and the internal portions which still exist in the liquid state are run out. By operating in this way, crystals of considerable size, though rarely possessing sharp and well-defined edges, will be found lining the cavity from which the fluid metal has been removed. Tin may likewise be deposited from its solutions in a crystalline state, by electric agency, and is by this means obtained in the form of elongated and very brilliant prisms, of which the exact relations have not been accurately determined.

TIN.

The tin of commerce is never quite pure, but is contaminated by the presence of various other bodies, and particularly arsenic and tungsten. To obtain it in a state of chemical purity, granulated tin, or tin-filings, may be oxidised by an excess of nitric acid, and the resulting stannic acid washed first with hydrochloric acid, and subsequently with water.

The peroxide of tin thus obtained is now reduced to the metallic state by being subjected to a low white heat in a closed crucible lined with charcoal. If pure water, instead of hydrochloric acid, be used for washing the peroxide, it is liable to retain traces of copper held in combination by the stannic acid.

Tin is not usually affected by exposure to the air at ordinary temperatures, but when fused its surface is rapidly covered with a pellicle of a greyish colour, consisting of a mixture of the protoxide of the metal with stannic acid.

This oxidation of tin proceeds with much greater rapidity at more elevated temperatures, and when heated to whiteness becomes so active as to be attended with distinct combustion, accompanied by a strong white flame. At a red heat it is oxidised by contact with watery vapour, and is rapidly converted into the peroxide with the evolution of hydrogen gas.

It is dissolved in concentrated hydrochloric acid, with the production of hydrogen gas. Similar results are obtained when it is acted on by warm dilute sulphuric acid, but the action is in this case extremely slow. Concentrated sulphuric acid acts energetically on metallic tin, with the formation of sulphate of the protoxide, and the evolution of sulphurous acid gas. Nitric acid readily oxidises tin, and converts it into stannic acid. If the acid employed be moderately concentrated, large quantities of deutoxide of nitrogen are evolved. When, however, very dilute acid is used, the oxidation is slowly effected, and no gas is given off, since by the mutual decomposition of the metal and nitric acid, peroxide of tin and nitrate of ammonia are simultaneously produced. If a fragment of metallic tin be placed in a vessel containing monohydrated nitric acid, that is, acid at its utmost state of concentration, it is not in the slightest degree acted on, but retains its. brilliancy of surface as perfectly as if merely exposed to atmospheric influences. On the addition, however, of a few drops of

water, a violent action on the metal is instantly set up, and a large portion of the liquid is frequently carried over the sides of the vessel by the rapid escape of the gases evolved. Tin is likewise readily attacked by aqua regia, which, if the hydrochloric acid be in excess, gives rise to the formation of a perchloride of the metal.

Water is decomposed by tin in the presence of the fixed alkalies; as, on heating this metal in a concentrated solution of either potash or soda, hydrogen gas is evolved, and a stannate of the base obtained.

### ORES OF TIN.

Oxide of Tin; Etain oxydé: Zinnstein.—The tin of commerce is exclusively obtained from the native oxide of that metal, which belongs almost exclusively to the primitive formations, and is chiefly met with in veins traversing granite, gneiss, and mica slate. Oxide of tin belongs to the right prismatic system, and has a specific gravity varying from 6.3 to 7.1. Its colour is usually brown or black, but sometimes red, grey, white, or yellow. It has an imperfect conchoidal fracture, a grey streak, and a highly adamantine lustre.

When pure, this mineral consists of tin 78.62, oxygen 21.38. It is, however, frequently associated with other metals, and often contains arsenic, tungsten, a little oxide of iron, and, more rarely, oxide of columbium.

A specimen of oxide of tin from Cornwall, analysed by Klaproth, gave the following results :---

Tin		77.50
Oxygen .		21.50
Oxide of iron		0.25
Silica	10408.	0.75
		100.00

The composition of this mineral, as well as that of artificial stannic acid, may be expressed by the formula SnO<sub>2</sub>. The most commonly occurring crystals are square-based prisms terminated by four triangular faces, which may be more or less modified on their edges and angles. It sometimes also affords modifications which give rise to the formation of eight terminal planes at each summit, which may also be themselves modified.

Peroxide of tin very frequently affords crystals curiously grouped together.

Oxide of tin is infusible when heated alone before the blow-

pipe, and is not readily reduced to the metallic state without the aid of fluxes. It is also insoluble in acids; but when heated on a charcoal support, with the addition of carbonate of soda, readily affords minute globules of metal.

Cornwall is one of the most productive localities of this mineral, where it occurs associated with copper and iron pyrites, wolfram, topaz, mica, talc, and tourmaline, together with axinite, and other silicates. Tin mines are also worked in Saxony, Austria, and Bohemia, Malacca, Peru, in China, and especially the Island of Banca in the East Indies, from whence large quantities are annually imported into this country. This oxide also occurs in Galicia, Spain; at Dalecarlia in Sweden; in the Department of the Haute Vienne in France; in Greenland, Russia, Brazil, Mexico, Chili, and the United States of America.

**Tin Pyrites**; *Etain sulfuré*; *Zinnkies.*—This mineral has hitherto been only found in a crystalline state in Huel Rock Mine, in the parish of St. Agnes, Cornwall; from whence cubical crystals, possessing cleavages parallel to the faces of the primitive form, have occasionally been obtained. Tin pyrites is of a yellowishgrey colour, and has a strong metallic lustre: it commonly occurs in granular amorphous masses, and has a specific gravity of 435. It affords a black streak, and presents an uneven fracture. When heated before the blowpipe, sulphide of tin fuses into a black slag, which is extremely difficult of reduction. It is soluble in nitric acid, with evolution of nitrous acid fumes, and affords on subsidence an abundant white precipitate of peroxide of tin. Two analyses of this substance yielded the following results :—

		Kudernatsch.				K	laproth.
Tin .			25.55				26.5
Copper	· .		29.39				30.0
Iron .			12.44		•	•	12.0
Sulphur	•		29.64				30.5
			97.02				99·0

The composition of this mineral, as far as concerns the state of combination of its elements, is still to some extent uncertain; although it would appear to be a sulphide in which the ratio of the sulphur to the whole of the metals present is as 1 : 1, and may be consequently expressed by the formula (SnCuFe)S. This mineral does not occur in sufficient quantity to admit of being metallurgically treated, and cannot, therefore, be regarded as an ore of tin.

**Mechanical Preparation of Tin Ores.**—The tin ore of commerce is found, either in regular veins or lodes, or in stockwerks, which are reunions of numerous small veins frequently crossing each other in all directions. When the ore occurs in lodes, it is extracted and brought to the surface by the methods described in the chapter devoted to the explanation of these operations; but the stockwerks, or minute metalliferous veins, which frequently traverse granite and the feldspar porphyry, called in the West of England *elvan*, are sometimes removed by large open workings, as at Carclaze Mine, in the neighbourhood of St. Austell, from which large quantities of tin are extracted by this method.

The principal tin mines of the West of England are grouped in three separate districts—namely, in the south-western part of Cornwall, beyond Truro; in the immediate neighbourhood of the town of St. Austell; and in the vicinity of Tavistock, in the county of Devon. The ore extracted from mines is commonly much disseminated in the gangue by which it is accompanied, and consequently requires to be reduced to a very fine powder before it can be separated from the earthy impurities.

From the high specific gravity of oxide of tin, its purification is, however, readily effected, as, from this circumstance, it is but little liable to be carried off by the washings to which it is subjected, and therefore admits of being almost completely separated from the various lighter bodies with which it is intermixed. The sulphides and arsenides which are found in veins producing tin ore do not admit of being readily eliminated by this treatment, as, from their high densities, they are liable to remain mixed with the ore at the close of these operations. This difficulty is remedied by a gentle calcination and rewashing of the ores, as the oxide of tin remains unaffected when moderately heated, whilst the associated sulphides and arsenides are decomposed, and their gravity thereby so diminished as to admit of their ready separation when again exposed to the action of a current of water.

On arriving at the surface, the ore, or work, is cleansed from the adhering clay and dirt by being placed beneath a small stream of water, by which the lighter portions are carried off in suspension. The ore, for this purpose, is sometimes placed on an iron grating beneath a fall of water, and is moved about with a large rake, to facilitate the operation. The ore, after being thus cleansed, is *spaled*, or broken with large hammers into pieces of from two to three pounds in weight; and these are subsequently divided, according to their richness, into three distinct classes.

The first, which is composed of the richest and purest fragments, is called *best work*, and is reserved for a separate mechanical preparation. The second class includes those portions which, although less rich, and contaminated with a larger amount of impurities, may, notwithstanding, be treated with advantage. The third division consists of the entirely sterile pieces, which are chiefly composed of stony gangue, and of iron and arsenical pyrites. When lodes at the same time yield ores of both copper and tin, they are as far as practicable separated during the sorting above described, and thus give rise to the formation of one or more additional classes.

The ore is now stamped, or reduced to a more or less minutely divided powder, under a series of heavy iron pestles, moved either by steam or hydraulic power. The size of the fragments of sand produced is regulated by the dimensions of the holes pierced in pieces of thin sheet iron inserted in front of the stamp cistern, and through which the pulverised mineral from the mill is carried by a strong current of water admitted into the stamps case for that purpose. The bottoms of the troughs are formed of siliceous rocks, firmly beaten into the earth by the action of the pestles; and the ore, on issuing from the stamps, is carried into a series of basins, in the first of which the richer and coarser fragments are deposited, whilst the poorer and more finely divided portions are collected in other reservoirs.

The rougher particles are washed and concentrated in buddles and *tossing tubs*, and the slime, or more finely powdered sand, in *trunks*, and on the rack.

When the ores have by these means become sufficiently concentrated, they are removed to the burning-house, where the sulphides and arsenides are decomposed by being roasted in properly constructed reverberatory furnaces. These are from 12 to 15 feet in length, and from 7 to 9 in width. The hearth is horizontal; and the arch, which is about 2 feet in height in the neighbourhood of the fire-bridge, sinks gradually towards the chimney. This arrangement is provided with but one opening, closed by an iron door placed at the extremity of the sole farthest removed from the grate, and immediately under a brick hood, by which the sulphurous and arsenical fumes are directly carried off into the chimney, without any annoyance or injury to the workmen.

In connection with the flues of these furnaces are large condensing chambers, in which the arsenious acid is deposited in a crystalline form. This is subsequently purified by a second sublimation, in order to convert it into the white arsenic of commerce.

From six to ten cwts. of ore constitute a charge for one of these furnaces, and this requires from twelve to eighteen hours, according to the amount of pyrites present, before it is sufficiently roasted. The charging of the furnace is effected by a small iron hopper placed in the centre of the brick dome; and as soon as the proper quantity of ore has been introduced, it is regularly spread over the surface of the sole, and the working door immediately closed. At the commencement of the operation the heat is very gradually raised until it reaches dull redness, at which temperature it is afterwards kept during several successive hours. At proper intervals during the process of calcination, the door is opened, and the mineral moved about with an iron rake, so as to expose a new surface to the action of the heated air passing through the furnace. When much pyrites is present in the ore, great care is required at the commencement of the operation to so moderate the temperature as to prevent its aggregation into large masses.

When the ore has been sufficiently roasted, which is indicated by its ceasing to exhale white fumes, an iron plate fitted into the floor of the furnace is removed, and the charge, whilst still red hot, is raked through the aperture, and falls into an arched chamber placed beneath, where it is allowed to cool. The calcined ore is now again subjected to the process of washing; and the impurities, which have been mostly decomposed and transformed into peroxide of iron, are, from their reduced specific gravity, readily removed. When the original ore is much contaminated by copper pyrites, it is, after being carefully roasted, often allowed to remain for some time exposed to the atmosphere previous to being again washed, as the sulphides present are by that means partially oxidised and converted into sulphates, which, being soluble in water, are readily removed. If tin ores contain much copper, it is usual to place them, after their removal from the burning-house, in a vessel containing dilute sulphuric acid, by which the copper is readily dissolved, whilst the oxide of tin remains unaffected. After this treatment with sulphuric acid, the ore is washed in pure water, and, under the name of black tin, is ready to be transferred to the smelter. In some of the Cornish mines the tin ore is associated with wolfram (a double tungstate of iron and manganese), which, from its great specific gravity, cannot by any mechanical means be separated from the oxide of tin. The presence of this mineral is therefore extremely prejudicial, as it exerts an unfavourable influence on the quality of the metal produced. Until recently, no convenient method for the separation of these bodies had been employed; but by the process lately patented by Mr. Oxland, this is readily and completely effected. For this purpose, the mixture of tin ore and wolfram is, with a little carbonate of soda, heated to redness in a reverberatory furnace, when tungstate of soda is formed, and the oxides of iron and manganese are liberated. The tungstate of soda, which is a soluble salt, is readily removed by water, and,

after crystallisation, may be employed by calico printers as a mordant. The oxide of iron, and other impurities, are subsequently separated from the lixiviated ores by washing, as above described.

When tin ore is found in alluvial deposits, as in the Valley of Pentewan, and other localities in Cornwall and elsewhere, it is extracted by a series of open workings called stream-works.

The stanniferous deposits in these situations occur in the form of regular beds or floors, in which the oxide of tin is associated with coarse sand and numerous pebbles, which have apparently been rounded by the action of water. These, together with the associated sands, are washed under a current of water in a large wooden box called a *griddle*, and the metallic fragments classed in accordance with the amount of metal which they respectively contain.

The different classes,—except the first, *prills*, which are sufficiently rich to be at once treated for the metal they contain,—are stamped and concentrated by the usual routine of washing.

Stream tin is always much purer, and consequently more valuable, than that obtained directly from mines, as, by long exposure to air and moisture, the pyrites with which it was originally mixed has become oxidised and carried off in solution.

#### ESTIMATION OF TIN-SEPARATION FROM OTHER METALS.

This metal, although it is sometimes precipitated in the form of sulphide, is invariably estimated in the state of stannic acid. The sulphide is transformed into peroxide by being roasted in a small porcelain crucible until the whole of the sulphur has been expelled : a few drops of nitric acid are then added, and the crucible and its contents again heated to redness.<sup>1</sup> Tin is readily separated from the earths, as also from zinc iron, cobalt and nickel, by sulphuretted hydrogen. For this purpose the solution should be so made in hydrochloric acid as to form a protochloride, through which the sulphuretted hydrogen gas is passed in large excess. When the liquor contains in solution a sufficient amount of hydrochloric acid, the beaker in which it is contained is covered with a glass plate and allowed to remain in a warm place until the whole of the sulphide has been deposited. This is now separated by filtration, and converted into peroxide of tin by exposure to heat and the addition of a few drops of nitric acid. When copper is also present, which is frequently the case in tin ores, these two

<sup>1</sup> Stannic acid contains 78.61 per cent. of metallic tin.

metals will be precipitated together by the sulphuretted hydrogen; and to effect their separation, the mixed sulphides must after calcination be treated by nitric acid, which transforms the tin into the insoluble peroxide, whilst the copper is converted into a soluble nitrate. After filtration from the insoluble stannic acid, the copper may be precipitated and estimated according to the method described when treating of that metal.

The analysis of tin ores, and particularly the separation of that metal from silica, is best effected by the following method, for which we are indebted to Professor L. E. Rivot, of the Ecole des Mines. The mixture of tin ore and its siliceous gangue is first finely pulverised, and afterwards heated to redness, in order to expel any hygroscopic water which may be present. It is then, after being weighed, placed in a small porcelain trough, and introduced into a tube, either of porcelain or hard German glass. heated by a gas flame or a charcoal fire. A current of dry hydrogen gas, furnished by an apparatus applied to one of its extremities, is now made to slowly traverse the tube, care being at the same time taken to avoid any loss of the matter operated on by the mechanical action of the gaseous current. When the apparatus has been thus arranged, the tube is heated to dull redness, and the reduction of the oxide of tin takes place very rapidly. After having allowed the mixture to cool down to the temperature of the surrounding air in an atmosphere of hydrogen gas, the trough and its contents are removed from the tube, when the ore, unless it has been too highly heated, will be found in the form of a grey powder, without any admixture of metallic globules. If the mixture operated on consists entirely of tin and silica, it may now be again weighed; and from the loss experienced, which corresponds to the amount of oxygen combined with the tin, may be deduced with tolerable accuracy the weight. of that metal present. As, however, any error of weight in the oxygen would be considerably multiplied with regard to the metal with which it was combined, the metallic tin may be dissolved in aqua regia containing a large excess of hydrochloric acid, and the residual silica collected on a filter, dried, and again weighed, when the loss will represent the amount of oxide of tin originally present; and from this may be readily calculated the per-centage of the metal itself.

When other substances, such as iron and copper, are present in the ore, the weight of the tin cannot be determined either by the amount of oxygen abstracted, or by that of the residual silica. Although the weight of the siliceous gangue can be thus ascertained, the tin must be separated from the other metals in the solution, and estimated as peroxide by the usual methods of analysis. One great advantage of this method consists in its affording a ready means of separating oxide of tin from its siliceous gangue, which, by the usual processes, is an extremely difficult and complicated operation.

### ASSAY OF TIN ORES.

Oxide of tin, although completely reduced by charcoal at a white heat, has such a strong affinity for silica that the highest temperature which can be obtained from a wind furnace is necessary for their separation. For this reason all tin assays should be made in lined crucibles, and at the temperature employed for those of the ores of iron. If a tin ore, with the addition of a proper quantity of some reducing flax, were subjected to the degree of heat employed in an ordinary assay of copper ore, a portion only of the metal would be obtained, and a large quantity of unreduced oxide would, in combination with silica, be retained in the slags. If the proportion of silica be large in comparison with that of the oxide of tin, but little metal, if any, will be obtained; although the ore, when judiciously treated, may, in the large way, be capable of being worked with considerable advantage.

Before proceeding to the assay of a tin ore, it is necessary to free it, as far as possible, from the siliceous gangue with which it is associated; and this is effected by a somewhat similar treatment to that by which its purification and concentration are conducted on the large scale. With this view, the pulverised mineral is roasted with a small quantity of powdered charcoal, and afterwards washed in an evaporating basin, or some other convenient vessel, until all the lighter substances with which it was associated have been removed. In the Cornish tin mines a large sharppointed shovel is employed for this purpose; and, after each successive washing, the heavier portions remaining in the shovel are still further reduced in size by the use of a large hammer, of which the faces are slightly rounded and well polished. The object of the roasting in these manipulations is to decompose the pyrites, and other arsenical substances present, and which, from their greatly reduced specific gravity, are then readily removed in suspension by the water by which the washing is effected. In some metallurgic laboratories, and particularly in that of the Ecole des Mines at Paris, a kind of small hand shaking-table, called an augette, is employed for this purpose; but equally satisfactory results may be obtained by the skilful use of a small horn spoon or ordinary porcelain evaporating basin. Instead of resorting to these mechanical contrivances, the removal of the sulphide

of iron and arsenical pyrites may be much more thoroughly and expeditiously obtained by boiling the pulverised ore for a short time with a slight excess of nitro-hydrochloric acid, by which these substances are readily and completely dissolved, whilst the native peroxide of tin remains unattacked. When all chemical action on the ore has ceased, water is added, and the residue thrown on a filter, where it is carefully washed. After having been allowed to dry, the residue is next removed from the filter, and calcined in an open crucible with a wide mouth, for the purpose of removing any small quantities of sulphur which may result from the decomposition of the pyrites originally present in the mineral. The ore, after being thus prepared, either by washing only, or by washing aided by an attack, is reduced in a lined crucible, and at the same temperature as that at which iron assays are conducted. The nature and proportions of the fluxes employed will necessarily depend on the amount and composition of the gangue with which the ore is associated ; but, as this is in most instances highly siliceous, carbonate of soda and fused borax may be always employed with advantage. For ores of moderate purity, from 30 to 40 per cent. of a mixture of equal parts of borax and carbonate of soda will be found to answer extremely well; and equally good results are obtained by the addition of 40 per cent. of a flux composed of three parts of carbonate of soda and one part of finely powdered lime.

For the estimation of this metal when occurring in extremely poor ores, and particularly in the slags obtained from furnaces in which its metallurgic treatment is conducted, the method of M. Rivot is eminently adapted, and is perhaps the only process by which the exact amount of tin existing in the poorer slags can be readily ascertained.

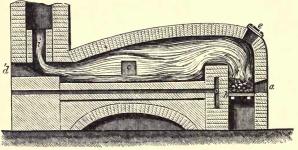
#### METALLURGY OF TIN.

The metallurgic treatment of tin ores is conducted by two different methods. By the first the reduction is effected in a reverberatory furnace fired with common pit coal, and in which the ores operated on are mixed with a proper amount of powdered anthracite or other carbonaceous matter. By the second process the oxide of tin is reduced in a small blast furnace, *fourneau* à *manche*, which is supplied with a current of air, either by bellows or blowing cylinders, and in which wood-charcoal is the only fuel employed. This method is merely applied to stream tin, and in those cases only in which extremely pure metal is required. The establishments in which the reverberatory furnaces are employed are called smelting-houses, and those in which the latter process is used are known by the name of blowing-houses.

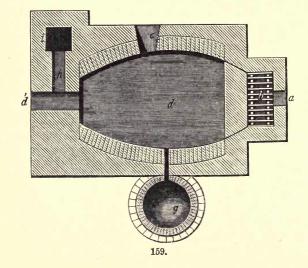
TIN.

# TIN-SMELTING IN THE REVERBERATORY FURNACE.

The metallurgic treatment of this metal in the reverberatory furnace includes two distinct operations—*smelting* and *refining*. The furnace in which the first of these processes is conducted is represented by the following woodcuts, of which fig. 158 is a vertical section, and fig. 159 a ground plan. a, is the fire-door by which coal is supplied to the grate, b; c, is the door by which



158.



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## TIN-SMELTING IN THE REVERBERATORY FURNACE. 403

the ore is introduced on the hearth, d; d', is the working door farthest removed from the grate; e, is a hole sometimes left in the crown of the vaulted roof for the purpose of introducing a current of air so as to carry the fumes into the chimney during the skimming of the slags from the metallic bath; o, is an air channel for admitting cold air beneath the hearth and through the fire-bridge, in order to prevent their becoming too highly heated during the progress of the operation; g, is an external basin into which the melted metal is drawn off; h, is the flue, and i, the chimney, which should be from forty to fifty feet in height. The roasted and washed ore is mixed, previous to its introduction into the furnace, with pulverised anthracite, and a small quantity either of slaked lime or fluor spar, which serves as a flux for the siliceous impurities present. Each charge consists of from 20 to 25 cwts. of ore, containing from 60 to 65 per cent. of metal.

First Operation .- Before the introduction of the ore into the furnace, it is carefully mixed with about 1-8th of its weight of pulverised coal or anthracite, and a little slaked lime, or fluor spar, is added to facilitate the fusion of the siliceous gangue. The mixture is also slightly sprinkled with water, for the double purpose of rendering it more easy to charge, and likewise to prevent any portion from being carried off mechanically by the draught into the flues. The charge varies with the dimensions of the furnace, within the limits already mentioned, and the heat is gradually raised. During the first six or eight hours the doors are all kept closely shut, and the contents of the furnace are consequently not stirred. At the expiration of this time the reduction of the oxide is complete, and the door, d', at the extremity of the longer axis of the furnace, is removed, and the melted mass worked up with a long iron paddle, in order to separate the metal from the slags, and to ascertain how far the reduction has become advanced.

When this is judged to be complete, the scoriæ are carefully withdrawn from the surface of the metallic bath by an iron rake, and removed by the door, d', to the floor of the building, where they are subsequently divided into three classes. The slags of the first class, a, which constitute about three-fourths of the whole weight produced, are as free from metal as it is possible to make them, and are consequently rejected as being of no further use. Those of the second class, b, are mechanically mixed with about five per cent. of tin, in the form of small metallic globules, which are afterwards extracted by crushing the scoriæ under a stamping mill, and separating by washing the metallic granules from the semi-vitreous matter with which it was associated. The slags constituting the third division, c, are much smaller in quantity than either of the two former classes, and consist of those scoriæ which are last removed by the rake from the surface of the metal previous to tapping into the exterior basin. This is extremely rich in metallic globules, and likewise contains some combined stannic acid: it is set aside to be remelted with the succeeding charge.

When the slags have all been withdrawn, and the metal alone remains in the furnace, the channel communicating with the external basin, g, is opened by removing the clay stopper with a pointed iron bar, and the tin immediately flows from the hearth into the outer basin, where it is allowed to remain a short time, in order that any portions of scoria still adhering to the tin may, from its less density, come to the surface and be skimmed off. When the tin has sufficiently settled it is laded into proper moulds, where it assumes the form of rectangular blocks.

The metal thus obtained is so much contaminated by other metals as to be rendered quite unfit for many purposes for which ordinary tin is employed. To get rid of these foreign matters, chiefly consisting of iron, arsenic, copper, and tungsten, together with some unreduced oxide of tin, the crude metal is now subjected to a process of refining.

Second Operation.—The refining of tin comprises two distinct operations, the first of which is a liquation conducted in a reverberatory furnace similar to that in which the reduction of the ore is effected; while the second, which may be called the refining proper, is characterised by the metal being caused to boil with great rapidity in an iron basin, by the introduction of billets of green wood.

For the liquation, or first stage of the process, the blocks of impure tin are arranged in the furnace so as to form a hollow heap in the neighbourhood of the fire-bridge, where they are gradually heated to the point of fusion. The tin now melts, and flows off the sole into the outer basin; but, after a time, the blocks cease to afford any more tin, and a residue consisting of a highly ferruginous dross remains on the hearth. Other blocks are now charged into the furnace, and the operation is continued until about five tons of metal have been collected in the basin. The ferruginous residue is afterwards removed, and set aside to be subsequently treated in connection with the stamped and washed scoriæ, b, of the smelting furnace, and the smaller amount of rich slags, c, which have been removed immediately from the surface of the bath before tapping the metal of the first fusion into the exterior basin of reception. The refining proper now begins. Billets of green wood are lowered by an iron gibbet into the bath of liquid metal, which, from the rapid evolution of gas thus pro-

duced, is kept in a constant state of violent ebullition. This brings to the surface a kind of froth chiefly composed of oxide of tin and other oxides, and causes the more impure and denser portions to fall to the bottom of the basin. This froth is removed by successive skimmings, and again thrown back into the furnace; and when the operation is thought to be sufficiently advanced, the green wood is withdrawn, and the contents of the basin allowed to settle. The metal now arranges itself into three distinct strata, of which the upper is the most pure; that in the middle is contaminated with small quantities of other metals; while the portions which sink to the bottom of the vessel are still more impure. When sufficient time has been allowed for this arrangement fully to establish itself, the different zones are successively laded out into iron moulds. The blocks first obtained are evidently the most free from impurities, and those taken from the bottom of the pot are so mixed with other metals as usually to require to be a second time heated in the reverberatory furnace in which the reduction of the ore is effected.

The operation of refining occupies about five hours; of which one is required to fill the basin, three for boiling the metal with green wood, and one for the subsidence of the bath and the casting into blocks.

Instead of causing an ebullition of the metal by the introduction of billets of green wood, the same effect is sometimes produced by an operation called *tossing*. When this process is employed, the agitation is caused by the workmen continually lifting in a ladle portions of melted metal which they let fall from a considerable height into the refining pot. The scum thus brought to the surface is carefully removed by skimming, and the metal afterwards allowed sufficient time to arrange itself in accordance with its purity and density.

Tin is usually cast into blocks weighing each about 3 cwts. The moulds in which these blocks are cast were formerly made of granite, but cast iron is now generally employed. The metal so moulded receives the name of block tin. The purer varieties are called refined tin, and are chiefly employed in the manufacture of tin-plate.

The treatment of tin ores gives rise to two distinct kinds of stanniferous residues, which require to be again reduced. The first of these consists of the slags b and c of the first operation; and the second, of the ferruginous dross found at the bottom of the furnace after the liquation of the crude tin previous to refining.

The slag, b, is stamped in a mill and washed, in order to effect the separation of the metallic globules which it contains. These are added to the scorize, c, in the state in which it is withdrawn from the furnace; and, on being again smelted, gives rise to the production of a certain amount of tin of inferior quality. The dross which remains on the sole of the furnace at the termination of the process of liquation is made to melt by the application of an increased temperature, and run off into a small basin totally distinct from the refining basin before described. After it has here been allowed to subside for a short time, the upper portions are laded into blocks as impure tin, which requires a second refining; whilst a white brittle alloy, with a crystalline fracture, adheres to the bottom and sides of the vessel. This is so contaminated with tungsten and other metals as to be of little By this method rather more than 30 cwts. of coals are value. required for every ton of metallic tin produced.

TIN.

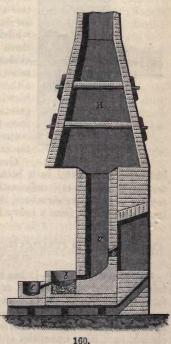
### SMELTING TIN ORES BY THE BLAST FURNACE.

These furnaces, which are not at present used in this country, were 6 feet in height from the bottom of the concave hearth to the throat, by which the ore and fuel were inserted. The tunnel-hole was placed at the origin of a flue, by which the metallic dust and fumes carried away by the blast were conducted into a chamber at the base of a high and narrow chimney, through which the smoke and gases generated escaped into the air. This chamber was not usually placed over the mouth of the furnace, but built behind it in such a way that the flue above the tunnel-hole might have a slightly inclined direction. The brick-work of the furnace was lined with an iron cylinder, which was itself internally cased with a coating of refractory clay, and had an opening in the side opposite the charging-hole through which were inserted two nozzles supplied by a cylinder blowing-machine set in motion by a water-wheel. The tuyeres were inserted at but a short distance from the sole of the furnace, which was gradually sloped down to a basin of reception of a circular form, and of which one part of the circumference entered beneath the sole of the cupola, whilst the other extended beyond it. At a short distance from this end, and at a lower level, was placed a second basin larger than the first, and from which the fluid metal might be conducted by a sloping gutter. Near this basin, and at a still lower level, was formed a third reservoir, in which was conducted the process of refining. The only fuel employed was charcoal, of which about 11 parts were required for the treatment of 1 part of washed ore. In smelting by this furnace it was necessary to keep it constantly filled with a proper admixture of ore and charcoal; and the reduced metal, which was received in the first basin, was subsequently run off into

the second, in which it was allowed to stand for some time; it then became divided by repose into layers of different degrees of purity. The scoriæ formed on the surface of the first basin were removed when sufficiently hardened, and then divided into two classes for subsequent treatment. Those containing metallic globules were stamped and washed; whilst those which retained tin in the state of combined oxide were simply broken with a heavy hammer, and subjected to a careful handpicking. The tin forming the upper zones of the second basin was considered sufficiently pure for the purpose of refining, and therefore laded into the third receptacle, where it was first subjected to ebullition by the introduction of blocks of green wood, and subsequently dipped out into moulds. The metal, which sunk to the bottom of the receiving basin, was also laded out to be a second time passed through the furnace; and, when very impure metal was obtained by the first operation, the entire charge was sometimes so treated.

The refining pot was usually made of cast iron, and kept warm by a small fire placed beneath it.

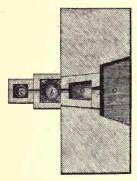
At the mines of Erzgebirge in Saxony, a blast furnace of about ten feet in height (figs. 160 and 161) is employed. The sides of the trunk, a, are formed of large pieces of granite; and the sole consists of a block of the same material hewn into the proper shape, and having a considerable fall towards the breast of the furnace. The fused matters escaping from this cavity flow continually into the exterior basin of reception, b, hollowed out of a mass of granite, and lined with a mixture of clay and powdered charcoal. This basin is furnished with a tapping-hole, by which its contents may be readily withdrawn into the small iron vessel, c. The charcoal and mineral are introduced by successive charges, and the combustion is accelerated by a blowing machine, of which the nozzle is introduced by the



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aperture, o. The slags produced float on the surface of the metal collected in the basin, b, from which they are removed by an iron crook as soon as they have become sufficiently consolidated. When the reservoir, b, has in this way become filled with metal. the tapping-hole is opened, and its contents are run into the vessel, c, where the process of refining is conducted by a vigorous ebullition induced by the use of a large pole of green wood, and the subsequent subsidence of the strata possessing different degrees of purity. The slags are divided into two classes : the richer are without any mechanical preparation fused with the succeeding charges of ore: and the poorer portions, after being stamped, are washed, for the purpose of separating the metallic granules which they invariably contain. The products of combustion are carried off by the chimney, H.

In working with the reverberatory furnace  $1\frac{1}{2}$  tons of coals are



161.

consumed for every ton of tin produced, and the loss of metal may be estimated at about five per cent. By this process every ton of tin smelted requires for its reduction  $1_{10}^{6}$  th ton of charcoal, whilst the per-centage loss of metal is three times greater. From this it is evident that the former is by far the more economical method of treatment. although the metal obtained from the blowing-house is, partly from the greater purity of the ore, and partly from the superior nature of the fuel, of better quality than that obtained by the other process.

Grain tin is prepared by heating blocks of that metal in a bath of melted tin; and, when the temperature has been sufficiently elevated to cause the block to assume a crystalline structure, it is withdrawn from the bath, and broken by a blow from a heavy hammer.

# PROCESS FOR THE PURIFICATION OF TIN AND MANUFACTURE OF ZINC WHITE.

Purification of Tin.-It has been long well known that a certain portion of the tin which comes into the English market is furnished by Peru. Of this tin some specimens are of tolerably good quality, and fetch prices nearly approaching to those realised by the less pure varieties of British tin. Others, on the contrary, contain such large quantities of tungsten, arsenic, and lead, as to

be almost useless for most of the purposes for which ordinary tin is employed. This impure metal sells for about  $\pounds 20$  per ton below the price of tin of the usual degree of purity.

After a series of investigations on the subject of Peruvian tin, I have been led to recommend the following method for its purification :---

The impure tin is first to be fused in an iron pot, and then granulated by being run off into cold water.

This granulated tin is now acted on by hot hydrochloric acid, care being taken that an excess of tin be kept constantly present. By this means the tin is dissolved in the state of protochloride, whilst the whole of the tungsten, which is the chief impurity of this metal, remains at the bottom of the vat in the form of a black powder.

The clear solution is then run off into another vessel containing a small quantity of the same impure tin in a granulated form, by which traces of arsenic and antimony which have not passed off in combination with the hydrogen evolved during the solution of the tin, are precipitated in the form of a black powder. Should any lead occur, it is at once removed by the addition either of sulphate of zinc or sulphuric acid.

From the clear solution thus procured the tin is obtained in the metallic form, and in a state of absolute purity, by the introduction of plates of metallic zinc, whilst a solution of pure chloride of zinc is produced.

The spongy metal thus thrown down, after being well washed, first in dilute hydrochloric acid, and subsequently in water, is fused in an iron pot and then cast into blocks, which will be as free from impurities as ordinary grain tin.

**Manufacture of Zinc White.**—The solution of pure chloride of zinc, obtained by the precipitation of tin by metallic zinc, is now decomposed by boiling with milk of lime. The lime employed for this purpose must be as free as possible from oxide of iron, and for this reason that obtained from the neighbourhood of Bristol is to be preferred.

The oxide of zinc thus precipitated, is entirely without the covering property known by painters under the name of body, but this quality is bestowed on it in a very eminent degree by its being heated to redness in a properly constructed furnace. The oxide of zinc thus obtained is found to be equal, if not superior, to ordinary zinc white.

# (410)

# ZINC.

## Equiv. = 32.52. Density = 7.0.

ALTHOUGH the ores of zinc have probably been employed from remote antiquity for the purpose of converting copper into brass, the metal itself does not appear to have been known in this country prior to the commencement of the sixteenth century; as we find it first mentioned by Paracelsus, who died in the year 1530.Its colour is blueish-white, and when recently broken, it presents a very brilliant crystalline surface. At ordinary temperatures zinc is a brittle metal, but when heated to between 212° and 300° it becomes both ductile and malleable. When the heat is increased to about 450° it is again brittle, and may at this temperature be readily pulverised in an iron mortar. Zinc fuses at about 773° Fahr., and when slowly cooled, exhibits a highly lamellar and crystalline texture. The zinc of commerce is never chemically pure, but is invariably contaminated by various other metals, such as lead, cadmium, iron, and copper: it may, however, be obtained in a state nearly approaching to purity by the following process :--- A fragment of the purest commercial zinc is dissolved in dilute sulphuric acid, and in the solution is placed a slip of the same metal, which is allowed to remain for some hours. The liquid is now filtered, decomposed by carbonate of potash, and the precipitate, after being well washed, is heated with powdered charcoal in an earthen or iron retort. The zinc, which is volatile at a white heat, is thus distilled over into a vessel of water placed beneath for its reception; but care must be taken that the neck of the retort be short and wide, as it will otherwise be liable to become choked by an accumulation of the condensed metal.

When a brilliant surface of clean and polished zinc is exposed to dry air, it remains unchanged at common temperatures; in a damp atmosphere, on the contrary, it is speedily tarnished, and soon acquires a grey colour from the formation of a superficial coating of oxide. When heated in contact with air at a temperature superior to that of its point of fusion, it takes fire, and burns with an extremely vivid white flame. The brilliancy of this flame is caused by the combustion of metallic zinc, which, giving rise to the formation of oxide of zinc, the *flores zinci*, or *nihilum album* of the early chemists, a body perfectly fixed at all temperatures, it becomes heated to whiteness, and thus communicates to the flame its peculiar intensity of colour. Oxide of zinc obtained by this means is largely employed when ground with oil as a pigment, in lieu of white lead, and from its perfect whiteness, as well as from the circumstance of its not becoming blackened by sulphuretted hydrogen, it is for many purposes to be preferred to the different preparations of the former metal.

Žine is dissolved in hydrochloric and dilute sulphuric acids with evolution of hydrogen gas; the action of these acids is more energetic on ordinary commercial zinc than on that which is chemically pure. This metal decomposes water with the formation of oxide of zinc and evolution of hydrogen gas. When the zinc is in a state of fine division, this reaction commences at a temperature slightly superior to 212°. Zinc is likewise soluble with the liberation of hydrogen gas in boiling solutions of potash and soda: in this case the oxide of zinc formed acts as a metallic acid. and combines with the alkaline base, forming soluble salts. If, at the same time that the zinc is inserted in the alkaline solution, a slip of iron be placed in contact with it in the same liquid, the decomposition of water may be readily effected at ordinary temperatures, as in this case the zinc alone is attacked, whilst the iron merely serves as the negative element of a voltaic pair by the action of which these decompositions are much facilitated. From the oxides of antimony, arsenic, tellurium, bismuth, cadmium, tin, lead, iron, cobalt, nickel, copper, mercury, silver, gold, platinum, palladium, rhodium, iridium, and osmium, dissolved in acids, zinc withdraws all the oxygen and precipitates the metals, whilst it is itself dissolved in the acid in the form of an oxide, and gives rise to the formation of salts of zinc.

From some of the higher oxides, when dissolved or diffused in acids, it withdraws only a part of their oxygen, and reduces them to the state of protoxides.

#### ORES OF ZINC.

Zinc usually occurs in combination with either sulphur, oxygen, carbonic acid, sulphuric acid, or silica, and is also occasionally found associated with alumina, as in a variety of the species spinel. Before the blowpipe the ores of zinc are almost completely infusible, but when strongly heated on a charcoal support, give off with greater or less facility white fumes of oxide of zinc, which are condensed on the cooler parts of the charcoal.

The zinc of commerce is chiefly obtained from the natural car-

bonates and silicates of this metal, and sometimes, although more rarely, from the oxide and the native sulphide or blende. The ores of zine occur either in veins traversing primitive or transition rocks, or in floors and stockwerks in more recent formations. The first mode of occurrence is by far the most frequent, but the more recent deposits are generally the most productive.

Red Oxide of Zinc; Zinc oxydé ferrifère; Zinkoxyd.—Red oxide of zinc, although rarely occurring in the crystalline form, has sometimes been met with in crystals derived from the right rhombic prism. It is found at Sparta in New Jersey, where it is associated with franklinite and carbonate of lime.

According to an analysis of Berthier this mineral is composed of—

Oxide of zinc	$ \begin{array}{c} \cdot & 88 \\ \bullet & \cdot & 12 \end{array} $
	100

Its specific gravity varies from 5.4 to 5.5; it has an adamantine lustre, and affords when scratched an orange-yellow streak. Its colour is red of various hues, sometimes inclining to yellow; it possesses two distinct cleavages at an angle of  $120^{\circ}$ , is brittle, and presents a conchoidal fracture.

Alone, before the blowpipe, this mineral is infusible, but with the addition of borax a yellow transparent glass is obtained. Its surface becomes dull, and ultimately white, by exposure. When acted on by nitric acid it dissolves without effervescence.

Red oxide of zinc is raised in large quantities in the locality in which it is chiefly found, and constitutes a valuable and abundant source of that metal. A specimen of this mineral, of extreme purity, and weighing 16,400lbs., was forwarded to the Great Exhibition of 1851.

Sulphide of Zinc; Zinc sulfuré; Blende.—This mineral occurs either massive or in dodecahedrons, octahedrons, and other allied forms. It admits of six distinct cleavages parallel to the faces of the dodecahedron, and when scratched affords a streak varying from white to reddish-brown. In colour it varies from resinyellow to dark-brown or black, and specimens having a green or red tint are occasionally met with. Its lustre is waxy or resinous, and when recently broken a brilliant and frequently submetallic surface is obtained. Specific gravity 4.0 to 4.1. Some specimens become electric by friction. This ore, particularly when of a dark colour, frequently contains sulphide of iron, and the red variety is sometimes associated with from 1 to 2 per cent. of sulphide of cadmium. When heated alone, or with the addition of borax, before the blowpipe, it is infusible; but when a charcoal support is employed, it yields white fumes of oxide of zinc.

Blende occurs in rocks of all ages, and is generally associated with the ores of lead, as also, though less frequently, with those of iron, copper, tin, and silver. The blende found in this country is, from the amount of sulphide of iron which it contains, usually of a dark colour, and hence called *Black Jack* by English miners. This sulphide is found abundantly in Cornwall, Cumberland, and Derbyshire, as well as in Transylvania, Hungary, and the Hartz.

A transparent variety of a bright yellow colour accompanies bournonite and fahlerz at Kapnick in Transylvania; still more beautiful specimens of an olive-green tint are procured from Schemnitz in Hungary; whilst Sweden, Bohemia, and Saxony, are famous for the brilliant brown and black crystals they afford.

The zinc and sulphur of which this mineral is composed are combined in the proportion of 1:1, and its composition will consequently be expressed by the formula ZnS.

Two analyses of this substance from different localities afforded to Berthier and Arfwedson the following results :---

Sulp	hide of zinc in c. Arfwedson.	Lameller from England. Berthier.				
Zine .	. 66.34	10.15	-		61.5	
Iron .	00				4.0	
Sulphur	. 33.66				33.0	
D-Uranization			1.		Contraction of the local	
	100.00				98.5	

From the difficulties experienced in its metallurgic treatment, this mineral was until recently but sparingly employed as an ore of zinc, although, when carefully roasted, it readily yields by distillation carbonaceous matter, a large proportion of the metal which it contains.

**Carbonate of Zinc**; Calamine; Zinc carbonaté; Zinkspath.— This substance is found in crystals in concretionated and compact masses, and in pseudomorphic forms. When pure, its colour is yellowish-white; but when much contaminated with iron, it is frequently brown or reddish-brown.

Its lustre is vitreous, inclining to pearly; streak, white; and cleavage parallel to the faces of the rhombohedron, which is its primitive form. Specific gravity from 4.3 to 4.45. Smithson, who analysed two specimens of this mineral from Derbyshire, found them to contain—

		I.		II.
Oxide of zinc		65.20		64.64
Carbonic acid	·	34.80	•	35.36
	Sh-	100.00	10	100.00

These numbers correspond to the composition represented by the formula ZnO,  $CO_2$ . It is soluble in acids with the evolution of carbonic acid gas, and when strongly heated before the blowpipe, carbonic acid is eliminated, and oxide of zinc remains. This is one of the most important ores of zinc, and, together with the silicate with which it is invariably associated, is extensively treated for the metal it contains. A compact, fibrous, semi-transparent variety of this mineral, of a pale-yellow colour, and disposed in concentric laminæ, occurs at Alston Moor in Cumberland, where it is found associated with blende and galena in a calcareous rock. It is likewise abundant in Derbyshire, as also in Siberia, Hungary, Silesia, Carinthia, and near Aix-la-Chapelle, as well as in many parts of the United States of America.

silicate of Zinc; Electric Calamine; Zinc oxydé silicifère; Zinkglas.—This mineral was for a long time confounded with carbonate of zinc, although they differ materially from each other, both in their chemical and physical properties. Silicate of zinc occurs stalactic, mammillated, botryoidal, and massive, and also crystallised in forms derived from the right rhombic prism.

Its usual colour is white, but blue, green, yellow, and brown specimens are occasionally met with. This substance may be either transparent or opaque, but has a vitreous lustre and white streak. Specific gravity 3.3 to 3.6. Fracture uneven. Crystals of this mineral when heated become electric, and the same effect is sometimes produced by friction alone. It consists of—

		m Limbo Berthier.	From Altenberg. Berzelius.					
Oxide of zine	з.	66.0					66.37	
Silica		25.0				ι.	26.23	
Water .		9.0	•	•		•	7.40	
						-		
		100.0					100.00	

These results indicate this body to be composed of two atoms of silicate of zinc united to one equivalent of water, and its constitution will consequently be represented by the formula 2 (ZnO, SiO<sub>3</sub>) + HO. This is a valuable ore, and is commonly associated with the carbonate of the same oxide in veins containing ores of iron and lead, together with the sulphide or zinc blende. Considerable quantities occur at Bleyberg and Raibel in Carinthia, as also at Freyberg, at Rezbanya in Hungary, Tarnowitz in Silesia, and Altenberg near Aix-la-Chapelle. Concentric botryoidal groups are also found in the Mendip Hills, and at Wanlockhead in Dumfriesshire; pseudomorphous crystals of the same substance occur in some parts of Derbyshire, and at Schemnitz in

#### ESTIMATION OF ZINC-SEPARATION FROM OTHER METALS. 415

Hungary. Before the blowpipe it decrepitates, intumesces, and loses its transparency. When reduced to fine powder, it is soluble in hydrochloric and sulphuric acids when gently heated, and on cooling the silica is deposited in a gelatinous state.

sulphate of Zinc is not found in sufficient quantity to be regarded as an ore of zinc. It is commonly associated with blende, by the oxidation of which it is supposed to be produced; it is a soluble salt of a white colour. It occurs at Holywell in Wales, in the Hartz, at Fahlun in Sweden, and Schemnitz in Hungary.

### ESTIMATION OF ZINC-SEPARATION FROM OTHER METALS.

For the purposes of analysis, zinc is commonly weighed in the state of oxide. If the solution of oxide of zinc is free from any admixture of ammoniacal salts, carbonate of soda may be at once added, and the liquor briskly boiled until the whole of the carbonate of zinc has been precipitated. This is afterwards collected on a filter, washed, and after being allowed to dry, calcined in a platinum crucible for the purpose of expelling the carbonic acid. If, on the contrary, ammoniacal salts are present, it is necessary that these should be first eliminated by the addition of an excess of carbonate of soda, and subsequent evaporation to dryness. The dry mass is then treated with boiling distilled water, and the precipitated carbonate of zinc separated by filtration.

Oxide of zinc may be separted from peroxide of iron, when the latter is in large excess, by the supersaturation of the liquid by ammonia. When thus treated the oxide of zinc remains in solution, whilst the peroxide of iron is precipitated, and must be thrown on a filter and washed. After having separated the iron from the solution by filtration, the zinc is obtained by the addition of an excess of carbonate of soda and evaporation to dryness. This method of separation is, however, only applicable in cases where small quantities of these bodies are to be separated, as, when considerable weights of the mixed oxides are to be dealt with, the oxide of iron invariably retains a notable weight of zinc. Under these circumstances, succinate of ammonia should be employed, care being previously taken to add to the solution a sufficient amount of caustic ammonia to determine the precipitation of a small portion of the oxide of iron.

Zinc may be separated from copper by passing through their acid solution a current of sulphuretted hydrogen gas, by which the latter is precipitated.

The best method of separating the oxides of zinc and manganese consists in transforming them into acetates, and adding to their solution a considerable amount of free acetic acid: sulphuretted hydrogen gas is now passed through the solution, and the zinc is precipitated in the form of sulphide, whilst in the presence of the free acetic acid the manganese is retained in solution.

Oxide of zinc is separated from lead either by a current of hydrosulphuric acid, as in the case of copper, or by adding to their solution in acids sulphuric acid, or an alkaline sulphate, when sulphate of lead of a white colour will be precipitated.

The separation of oxide of zinc from alumina is effected either by their solution in an excess of caustic potash, and the precipitation of the zinc by sulphuretted hydrogen, or by converting them both into acetates, when the same reagent causes the precipitation of the zinc in the form of sulphide.

To separate oxide of zinc from magnesia, a sufficient quantity of chloride of ammonium to prevent the formation of a precipitate on the addition of ammonia, is added to the solution. When the liquor is strongly acid this precaution may be omitted, and, on passing a current of sulphuretted hydrogen, a precipitate of sulphide of zinc at once takes place. The filtrate from the zinc precipitate is afterwards rendered acid and evaporated, and from this the magnesia may be separated by the usual method.

Lime is separated from oxide of zinc by first rendering the liquor ammoniacal, and afterwards precipitating the lime by oxalate of ammonia. The zinc is obtained from the filtrate by the addition of carbonate of soda and evaporation to dryness. On treating the residue with boiling water, the carbonate of zinc remains undissolved, and is converted into oxide by calcination at a high temperature in a porcelain crucible. Every 100 parts of the oxide thus obtained correspond to 80.26 parts of metallic zinc.

# ASSAY AND ANALYSIS OF THE ORES OF ZINC.

The estimation of the amount of zinc contained in an ore of that metal, is by the dry way a very troublesome and uncertain operation, as the zinc which it contains, from being extremely volatile, and subject to oxidation at high temperatures, cannot be obtained in the form of a button as is the case with the metals heretofore described, and must therefore be distilled and again collected in proper receivers, or its weight must be calculated from the loss experienced by its ores when subjected under certain circumstances to an elevated temperature. Berthier, who has made numerous experiments on this subject, divides all bodies containing zinc capable of being assayed by the dry way into the four following classes:— 1st. Those in which the metal exists in the form of oxide uncombined with silicic acid.

2nd. Ores of zinc in which the metal is present as oxide, wholly, or in part combined with silicic acid.

3rd. Zinc ores in which the metal is wholly or in part combined with sulphur.

4th. Alloys of zinc.

To reduce the oxide of zinc contained in minerals of the First Class, it is only necessary to mix them with powdered charcoal, and expose them for a sufficient time to a white heat. The metal thus obtained is at the moment of its reduction converted into a vapour readily condensible in proper receivers, and if, therefore, the operation be conducted in an earthen retort, with a long beak kept properly cooled, the whole of the metallic zinc may be collected and weighed. To do this the neck of the distillatory apparatus must be broken off, and its lining of metallic zinc carefully detached : but this method of estimation is from two distinct causes liable to be inexact. The first of these is, that the metallic deposit is extended over a large surface, and is frequently very difficult to detach completely from the sides of the retort to which it firmly adheres; and, secondly, as the neck of the retort is open during the operation, all the vapour which approaches nearest to the orifice becomes converted into oxide. The removal of the metallic crust from the interior of the neck is much facilitated by the application of a little plumbago previous to the introduction of the charge. When the beak is not of itself sufficiently long for the complete condensation of the zinc, a piece of glass tube may readily be adapted so as to lengthen it. If the coating adheres so firmly as not to admit of complete removal, that which remains attached to the retort may be dissolved in nitric acid, which, on being evaporated to dryness, and calcined, yields a certain amount of oxide, four-fifths the weight of which must be added to that of the metallic zinc scraped from the fragments of the broken retort.

Instead of operating in this way, an approximation to the quantity of zinc contained in an ore may be obtained by heating it together with proper fixed fluxes in a lined crucible at the temperature of an iron assay, and afterwards judging of the amount of zinc present from the loss of weight experienced during the operation. The resulting button, which is a mixture of slag and granules of cast iron, is first weighed without being broken, and after crushing it in an iron mortar the metallic shot are removed by a magnetic bar. The weight of these is next ascertained, and by difference, that of the scoria is readily found. The weight of the oxygen lost by the iron during its reduction is now by calculation added, and on subtracting the product of these united numbers from the amount of flux and mineral employed we immediately get the weight of the volatilised zinc.

By deducting, on the other hand, the weight of the fixed flux used from that of the slag obtained, the weight of the earthy matter and unreducible oxides associated with the ore of zinc may be arrived at with a tolerable degree of precision.

These results have been expressed by Berthier in the following tabular form :---

Let W be the weight of crude ore, and w that of the ore after calcination; t the weight of the flux added; f the weight of the cast iron found; s the weight of slag; o the weight of oxygen combined with the iron; and z the weight of the oxide of zinc sought.

Then we have-

W crude ore = calcined do. = wt fixed fluxes added . . . . t

Gives Metal fSlag sOxygen oTotal f + s f + s + oOxide of zinc w + t - f - s - o

Flux added t

Earthy matters s - t.

Ores of the Second Class.—The silicates of zinc not being reducible by charcoal alone, require the addition of some flux capable of combining with the silicic acid present. For this purpose lime or magnesia may be advantageously employed, and the ores are then treated precisely like those belonging to the first class.

The Assay of Ores belonging to the Third Class is conducted, after the removal of their sulphur by a careful roasting, precisely like those of the first and second.

Fourth Class. Alloys of zinc with iron, copper, or tin, may be assayed by heating them in a lined crucible with an earthy flux, and weighing the resulting button: the loss experienced will in this case very closely approximate to the amount of metallic zinc originally present.

Analysis of Zinc Ores.—Carbonate of zinc may be analysed by the following process:—To ascertain the amount of water which it contains, a weighed quantity is heated in a short combustion tube, to which a chloride of calcium tube is attached; when the increase of weight experienced by the latter represents the amount of water contained in the quantity of substance operated on. Another weighed quantity of the mineral is now strongly heated in a platinum crucible: the loss experienced in this case corresponds to the united weights of water and earbonic acid contained in the ore. By deducting the first of these results from the second, we readily ascertain the weight of the carbonic acid originally combined with oxide of zinc. Either a fresh portion of ore, or the residue of the above calcination, is dissolved in hydrochloric acid, evaporated to dryness, and subsequently treated with hot water, by which the soluble salts are readily taken up, whilst a certain portion of insoluble silica which remains is collected on a filter and carefully washed. Excess of ammonia is now added to the filtrate, and the precipitate formed separated by filtration. The liquor, which in this stage of the operation passes through the filter, contains the whole of the oxide of zinc, which may be separated and estimated with the precautions already described.<sup>1</sup>

When blende is the mineral to be examined, it may be directly treated with aqua regia, and the zinc and other metals estimated precisely as when a carbonate has been operated on. A separate quantity of the ore must be attacked for the estimation of sulphur which is precipitated and weighed in the state of sulphate of baryta.

#### METALLURGY OF ZINC-ENGLISH PROCESS.

The metallurgic treatment of the ores of zinc is extremely simple. When calamine is the mineral operated on, it is first submitted to a calcination, by which it is rendered friable, and its water and carbonic acid expelled. The roasted ore is afterwards reduced under heavy edge-runners to the state of fine powder, and mixed with a proper proportion of charcoal or coal dust, by which, when strongly heated in earthen retorts, its conversion into metallic zinc is determined. The reduction of the oxide is effected at the expense of the carbon present, carbonic oxide gas is evolved, and the metallic zinc liberated is condensed in proper receivers adapted to the retorts in which the operation is conducted. The arrangement of the apparatus in which these transformations take place is varied in different localities in accordance with the qualities of the mineral treated, and the nature of the fuel employed.

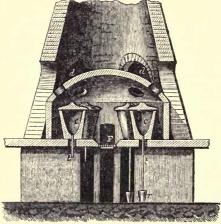
In this country the greater part of the zinc works are situated in the neighbourhood of Bristol and Birmingham, but a few furnaces are also found in the vicinity of Sheffield. Bristol and Birmingham are chiefly supplied with ores from the Mendip Hills and Flintshire; and Sheffield from the mines of Alston-moor, in Cumberland. The ore most commonly employed is calamine,

This process, though not absolutely accurate, is sufficiently so for practical purposes.

which, after being carefully freed from galena by hand-picking, is calcined, before its introduction into the smelting apparatus, by being exposed, after being broken into a coarse powder, to the action of a large reverberatory furnace with a low dome. In some instances this calcination is omitted, and the calamine is then at once broken into fragments of the size of hazel nuts, and mixed with its due proportion of small coals.

Sometimes, though more rarely, blende is employed. For this purpose it is broken into pieces of the size of a filbert, and roasted, without further preparation, in large reverberatory furnaces, heated by a coal fire. These are about 10 feet in length and 7 in width; the distance between the sole and roof at the highest part being 30 inches, and the height of the fire-bridge 18. The blende is laid on the bottom of the furnace in a layer of from 3 to 5 inches in thickness, and is constantly kept stirred with iron rakes during the operation. The roasting of each charge occupies from 10 to 12 hours, and the loss of weight sustained during the calcination amounts to about 20 per cent.

The process employed in this country for the reduction of ores of zinc is called *distillation per descensum*, and is conducted in a furnace in many respects very similar to those used in glass-houses



162.

for the fusion and preparation of glass. These furnaces may be either square or round, but that represented, fig. 162, and which is usually preferred, has the latter form. The fire-place, F, is raised to a convenient height above the surface of the ground, and is situated in the centre of the arrangement. Around this are disposed the crucibles, c, into which is charged the mixture of ore and fine coal from which the zinc is to be distilled.

The dome, d, is pierced with openings, by which the mixture of powdered ore and coal is introduced, corresponding to each crucible, and the bottom of each pot is furnished with a hole in connection with an iron tube, t, which traverses an opening left in the sole of the furnace, and thus projects beneath the floor into a chamber placed immediately below it. The upper orifice of this tube is closed, previous to the introduction of the charge, by a wooden plug, which becoming converted into charcoal during the operation, is rendered sufficiently porous to admit of the passage of the vapour of zinc, but at the same time prevents the escape of the small coal and calcined mineral. Each crucible is covered with a lid, firmly secured in its place by a lute of fire-clay, and the distilled metal is condensed in the tube, t, and falls in the form of drops in the vessel, r, placed there for that purpose. As these tubes are liable to become choked by the condensed metal, it is necessary to clear them from time to time by the insertion of a long iron rod, since they might otherwise become entirely closed, and thus give rise to dangerous explosions. The zinc collected in this operation in the form of drops and very fine powder, mixed with a certain portion of oxide, is afterwards melted in a large iron pot, set in brick-work, and heated by a fire beneath. The dross which collected on the surface of the fused metal is skimmed off and returned into the crucibles in a succeeding operation, whilst the zinc itself is cast into rectangular bars or ingots, in which state it is sent into the market. Five distillations may be made by a furnace of this kind in fourteen days, in the course of which from 8 to 10 tons of roasted ore are treated, and from 20 to 25 tons of coals consumed. The metal obtained commonly amounts to from 35 to 40 per cent. of the ore treated, and the duration of each crucible may be calculated at about four months. The pots, when unfit for further service, are removed through apertures made in the surrounding brick-work. Before being set, they are heated to redness in a reverberatory furnace, and carried to their places by a pair of large iron pincers, slung in chains, and supported by a kind of overhead railway, as in the case of ordinary glass-house pots. When set in their places, the brick-work is repaired and a cover fitted in the usual way. At the close of each operation, the crucibles are discharged by removing from the bottom the condensing pipe, t, and withdrawing the residue through the aperture after breaking with a rake the piece of charcoal by which it was closed during the process of distillation. The metallurgy of zinc in this country is not, however, so extensively carried on as formerly, since, from the

large importations of this metal which annually take place from Belgium and Germany, its price has become so reduced as to afford but little profit to the British manufacturer.

### PREPARATION OF ZINC AT THE VIEILLE MONTAGNE.

The preparation of zinc at the Vieille Montagne, in the neighbourhood of Liege, is minutely described by Regnault in his Chimie Elémentaire, from which are gathered the following details :---The minerals employed are the silicate, carbonate, and oxide of zinc, which are sometimes compact and earthy, and at others crystalline and nearly pure. The gangue is almost exclusively composed of clay, which occurs in the form of amorphous masses, occupying cavities in the middle of the masses of calamine. In order that this may become softened and be readily removed, the mineral is left exposed to the air for several months before it is employed, by which treatment the greater part of the impurities becomes detached and carried away by the rains. When very impure, the mineral is sometimes washed under a stream of water, by which the clay is almost entirely removed. At this establishment the ore is divided into two classes, the white ore and the red, distinguished both by their appearance and their chemical composition. The second of these contains a larger amount of iron than the first, and is less rich in zinc, but is nevertheless more readily treated than the whiter variety.

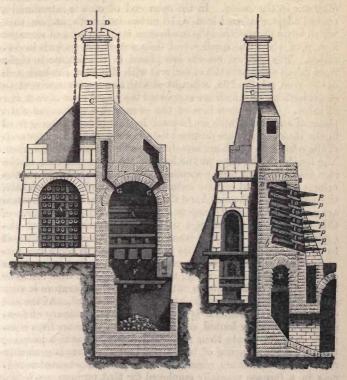
The white ore contains, on an average, 46 per cent. of oxide of zinc, and the red only 33. The peroxide of iron contained in these two ores amounts respectively to 5 and 18 per cent.

The mineral, after it has been washed, is calcined in conical kilns similar to those employed for burning lime. The ovens in which this is conducted are heated by two lateral fire-places, covered by an arch and provided with a flue, which is divided at a short distance from the hearth, and enters the kiln by twenty different apertures, arranged at regular intervals from each other. These openings are four inches square, and are lined with fire-bricks. At the bottom of the furnace are two rectangular openings, destined for the removal of the roasted ore after having passed through the higher and more intensely heated parts of the arrangement. Two slabs of cast iron, inclined at an angle of 45°, divide the descending column of ore, and facilitate its removal through the doors. The ore is charged by the mouth of the furnace, and the smaller and larger fragments are so mixed together as to allow a sufficient passage for the heated air and flame entering through the openings. By this treatment the mineral loses the whole of its water and the

# PREPARATION OF ZINC AT THE VIEILLE MONTAGNE. 423

larger proportion of its carbonic acid. The loss experienced is 25 per cent. The fuel employed is ordinary pit coal. This operation is continuous, and, in proportion as the roasted ores are removed from the lower part of the cone, fresh mineral is introduced by the upper opening, around which is a platform, where a supply is constantly kept in readiness.

The roasted ore, after its removal from the kiln, is ground under heavy edge-runners, sifted through very fine sieves, and sent to the furnace, in which its reduction is effected.



163.

164.

The reducing apparatus consists of four distinct furnaces united in one mass of brick-work. Each of these has the form of an arched recess, A, figs. 163 and 164, whose greatest height is 8 feet 8 inches above the surface of the floor. The back of this opening is composed of a brick wall, and is slightly inclined in the direction a b; the face, cd, is, on the contrary, left quite open for the introduction of the retorts. The fire-place, F, is placed beneath the surface of the ground, and the flame and heated air enter the interior of the furnace through four apertures, e. In the arch are placed two separate flues, G G, which terminate in a central chimney, c, divided into four compartments, and closed by dampers, D, corresponding to each division. In each of these furnaces are placed 42 cylindrical retorts, r, closed at one of their extremities, and made of refractory clay. These are 3 feet 8 inches in length, and 6 inches in diameter in the inside. In the open end of each is introduced a conical adapter of cast iron, o, 16 inches in length, and on this, which forms the mouth of the condensers, is fitted a cone of wrought iron, p, of which the smaller end does not exceed an inch in diameter. The earthen retorts are placed in the furnace in eight rows raised one above the other, and with this view the back wall of the oven, a b, fig. 164, is furnished with as many successive steps or projections, on which are supported the closed ends of each row of tubes. On the open face of the oven, c d, are arranged eight plates of cast iron, which are fastened in their places by being fixed in the masonry, and are destined for the support of the outer ends of the retorts, to which are attached the adapters already described. The height of the steps at the back of the oven, and that of the iron plates in front of the opening, is so arranged as to give to the retorts a slight and regular inclination downwards, by which both the distillation of the metal and the removal of the residual matters are much facilitated. During two months the firing of a furnace of this description is continued without intermission; but at the expiration of that time it is commonly found necessary to allow it to go out, in order to repair its internal lining. When a new furnace, or one which has been recently repaired, is first lighted, the open face of the arched cavity, A, is closely built up with bricks or fragments of broken retorts, after which the temperature is very gradually raised until a white heat has been attained. At the end of four days the furnace is considered, under ordinary circumstances, sufficiently heated, and the refractory tubes are then separately introduced into their respective places. For this purpose, the temporary stopping of bricks and broken retorts is gradually removed, and the tubes, which have been previously heated to redness in a furnace specially employed for that purpose, are introduced into their places. The interstices existing between the different tubes are now closed with fire-clay, so as to make good the front of the oven, and the cast and wrought iron adapters are secured in their places with a luting of the same material.

When the retorts are thus arranged in the oven, a small charge of powdered ore and charcoal is at first introduced : these are suc-

# PREPARATION OF ZINC AT THE VIEILLE MONTAGNE. 425

cessively increased until, at the expiration of three or four days, the apparatus has got into a regular way of working. At this point we will first investigate the operation of the apparatus. The mineral is brought to the furnace in wooden boxes, where it is mixed with fine coal slightly moistened with water. The charge of each oven consists of 1100lbs. of calcined calamine and 550lbs. of a bituminous coal, which has been previously reduced to the state of a fine powder. These substances are intimately mixed together before being introduced into the retorts. Before charging the tubes, the residue remaining from the preceding operation must be carefully withdrawn, and the inside of each retort, as well as of the iron adapters, be thoroughly cleaned with a small iron scraper. The charging, which usually commences at 6 o'clock in the morning, begins with the lower tubes. The mixture of ore and coal is introduced by the aid of a semi-cylindrical shovel attached to an iron rod as a handle; and as soon as the charging is terminated, the fire is increased by raising the damper on the top of the chimney and the addition of a fresh supply of fuel. After a short time, large quantities of carbonic oxide gas are evolved, which burns with a blue flame at the openings of the iron adapters. At the expiration of a further period, the brilliancy of the combustion is considerably increased, and the flame at the same time assumes a greenish-white tint, with the evolution of copious white fumes. The distillation of the metal now begins, and the conical tube of wrought iron is luted on. At this point the greatest care is requisite, in order to so conduct the fire that the heat of the tubes in every part of the furnace may be as nearly as possible equal; but, in spite of every precaution, those in the higher rows are invariably less heated than the others, and are consequently only charged with such ores as are most easy of reduction.

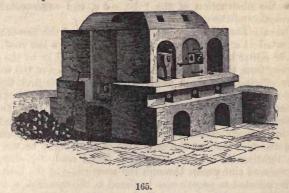
With this view, the retorts in the higher parts of the furnace are charged with the red variety of ore containing much iron, whilst the lower series is supplied with the whiter and more refractory kind. At the expiration of two hours, the workman removes the wrought iron adapter with a proper tongs, and strikes it sharply above a vessel in which is collected the oxide of zinc or *cadmie*, which is detached and reserved to be added to the mixture of ore and powdered coal in a future operation. When this has been done, an assistant holds a large iron ladle, called a *poêlon*, under the beak of each retort, at the same time that the foreman draws out into it with an iron scraper the distilled zinc, which accumulates in the liquid state at the shoulder formed by the junction of the clay and cast iron tubes. He also detaches with his rake the metal which has condensed in the form of drops on the inside of the iron cone. The liquid zinc thus collected in the poêlon is covered by a scum principally consisting of oxide of zinc, and which is removed before pouring the metal into moulds, where it receives the form of rectangular flat ingots, weighing from 75lbs. to 85lbs. each. When these operations are completed, the sheet iron cone is again luted on, and, after firing continuously for two more hours, another tapping is made in the same way, and a further supply of liquid zinc obtained. These manipulations are repeated at intervals of two hours until five o'clock in the evening, when the distillation is commonly terminated.

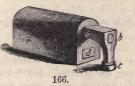
The tubes are now cleaned out, and entirely freed from any earthy residue, so as to be ready to receive the second charge, to which has been added the oxide of zinc formed during the progress of the preceding operation. In this way two charges of the furnace are worked off in twenty-four hours, which together furnish about 620lbs. of metallic zinc, and from 30 to 45lbs. of more or less oxidised granules. Calamine, when thus treated, yields about 30 per cent. of metal, and retains about 10 per cent. in the residue subsequently removed from the retorts. The zinc which is retained in the residue exists in the form of silicate of the oxide of that metal, which is not to be reduced at any temperature by the action of charcoal alone.

A large proportion of the zinc annually produced is employed in the form of thin sheets. For this purpose it is necessary to again melt the ingots, directly obtained by the treatment of the ores, as above described. This is effected in a reverberatory furnace with an elliptical hearth, having a slight inclination towards one side. At the lowest point of the sole, which is made of refractory clay, is placed an hemispherical reservoir, in which the fused metal is collected, and the ingots to be remelted are introduced through one of the doors and piled near the fire-bridge on the highest part of the hearth. The melted zinc is dipped out of the sunk reservoir with iron ladles, and poured into moulds of various dimensions in forms convenient for the purpose of rolling into sheets. These plates are subsequently reheated in a second furnace built in the same mass of brick-work as the first, and which is merely heated by the waste gases escaping from it. Here they are elevated to a temperature not much exceeding 212°, and are then passed through the rolling mill, by which they become reduced to the form of leaves, having various degrees of thickness.

#### SILESIAN METHOD OF ZINC-SMELTING.

In Upper Silesia, where large quantities of zinc are annually produced, the apparatus employed in its metallurgic treatment differs materially from that in use at the Vieille Montagne and in other parts of Belgium. Fig. 165 gives a general idea of the appearance of a Silesian zinc furnace. The distillation is conducted in muffle-shaped retorts, R, figs. 166 and 167, of about 3 feet 6







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inches in length, and 1 foot 8 inches in height. The anterior face of these is pierced with two openings, a and d, by the first of which is attached an earthen tube,  $a \ b \ c$ , bent at right angles through which the reduced metal is sublimed; whilst the second, which serves for the withdrawal of the fixed residue, is closed by a stopper of baked clay, and securely luted. The muffles are made in moulds, and composed of a mixture of well-kneaded fire-clay and finely ground potsherds. The metallic zinc is collected either in small cast iron pans or in vessels of baked clay.

From six to ten of these retorts are symmetrically placed in two rows on either side of the central hearth, and are introduced into the laboratory of the furnace through arched apertures left in the brick-work of its sides for that purpose. These openings are subsequently closed by iron plates so placed as to prevent the too rapid cooling of the bent arms,  $a \ b \ c$ , whilst the aperture, b, through which the charge is introduced, is readily accessible by a smaller door, e, turning on hinges, and provided with a spring fastening. The fuel consumed on the grate,  $\mathbf{F}$ , is pit coal, and the retorts are charged with a mixture of equal volumes of roasted calamine and the fine cinders which have fallen through the grate. These are for this purpose preferred to powdered pit coal, because the latter is, from the quantity of tarry matter evolved, liable to cause the obstruction of the tube, a b c, and consequently, an interruption of the operation.

The calamine, which is introduced in pieces of the size of a pea, is roasted in a large reverberatory furnace with a low roof: this may be either heated by a separate fire of pit coal, or by the gases escaping from the apparatus in which the reduction of the roasted ore is effected. When a newly-erected furnace is first lighted, great care is necessary to prevent the cracking of the retorts and the too great expansion of the surrounding brick-work. During the first two days the fire is applied under the grating, and the heat is gradually raised to redness : after this, the fuel is placed on the grate itself, and, at the expiration of from eight to ten days from lighting the fire, the retorts are found ready for charging. The reduced zinc passes through the aperture, c, of the bent arm, and is collected in proper vessels placed in the openings, o, left in the brick-work of the furnace. Each operation requires twenty-four hours for its completion, and the residue, which is a greenish semi-fused mass, is only removed after every third distillation.

Besides being largely employed in the manufacture of brass, this metal is extensively used for making baths, water-tanks, spouts, pipes, plates for the engraver, for galvanic batteries, for covering sheet-iron (galvanised iron), roofing, and a great variety of other purposes, among which may be mentioned plates for the zincographer, the manufacture of white oxide of zinc, &c.

# BISMUTH.

## Equiv. = 70.95. Density = 9.8.

BISMUTH possesses a white-grey colour, but at the same time presents a distinctly red tint when compared with zinc, antimony, or one of the whiter metals. It is brittle, and consequently cannot be drawn out under the hammer, and when broken presents a highly crystalline fracture. Very beautiful crystals of this metal are readily obtained by fusing a considerable quantity in an earthen crucible, and afterwards setting it aside and allowing it to cool very gradually. For this purpose the ladle or crucible in which the fusion has been effected should be removed from the fire to a sand-bath, and covered with a hot iron plate on which are placed a few pieces of ignited charcoal. At the expiration of a certain time, the external crust of solidified metal is pierced with a hot iron, and the interior portions, which still retain the liquid form, are rapidly poured out.

The upper crust is now removed, and beautiful crystals of bismuth are found coating the sides of the vessel. These are in the form of cubes, or hollow tetrahedrons, and from a slight covering of oxide varying in its thickness, assume very beautiful prismatic colours.

Commercial bismuth is never absolutely pure, but as the other metals with which it is associated are commonly more oxidisable than itself, it may in a great degree be separated from them by fusing the powdered alloy in an earthen crucible, with one-tenth part of its weight of nitrate of potash. On heating this mixture until the nitre has been completely decomposed, a portion of the bismuth, together with the major part of the impurities, will have been oxidised, and remain in combination with the potash, whilst a button of purified bismuth collects in the bottom of the crucible. When an absolutely pure specimen is required, it can be prepared by fusing together a mixture of subnitrate of bismuth and black flux.

This metal fuses at a temperature of 476° Fah. It is volatile at a high heat, and may be distilled. Bismuth is placed by Faraday at the head of diamagnetic substances; it transmits heat less readily than most other metals. At a white heat,

#### BISMUTH.

bismuth boils, and is sublimed, and at this temperature is stated by Regnault to decompose the vapour of water: it is not affected by exposure to dry air, but when placed in a humid atmosphere gradually becomes covered with a thin pellicle of oxide. When strongly heated in air, bismuth burns with a bluish flame, and gives off fumes of a light yellow colour.

It does not decompose water in presence of the stronger acids, and is attacked with difficulty by concentrated hydrochloric acid. Sulphuric acid, unless concentrated and hot, does not attack it, and in this case sulphurous acid is evolved. Nitric acid attacks it with great facility with the formation of soluble nitrate of bismuth.

#### ORES OF BISMUTH.

Bismuth occurs native, and also in combination with sulphur, oxygen, silica, and tellurium. Its ores readily fuse before the blowpipe, and in the oxidising flame afford an oxide by which the charcoal support is stained of a brownish-yellow colour.

Native Bismuth; Bismuth natif; Gediegen Wismuth: crystallises in the cubic system but is also found massive, granular, reticulated, and arborescent. Colour silver-white, inclining to red; lustre metallic, and streak unchanged. Cleavage parallel to the faces of the octahedron. Frequently contains small quantities of arsenic, and is often associated with silver, and sometimes with iron.

Native bismuth accompanies various ores of silver, lead, zinc, cobalt, and nickel, and usually occurs in veins traversing either gneiss or clay-slate. Its principal localities are the silver and cobalt mines of Saxony and Bohemia, Altenberg, Schneeberg, Annaberg, Joachimsthal, and Johanngeorgenstadt. It is likewise found at Bieber, in the principality of Hanau, at Löling in Carinthia, and at Fahlun in Sweden. Native bismuth also occurs at Huel Sparnon, near Redruth in Cornwall, at Caldbeckfell in Cumberland, and near Alloa in the county of Stirling. Native bismuth supplies nearly the whole of this metal which is employed in the arts ; the greater portion is derived from the mines of Schneeberg in Saxony, where it is found associated with the ores of cobalt.

Bismuth is also found in combination with other bodies, but these compounds are by no means of common occurrence.

Sulphide of Bismuth occurs in Cumberland, Cornwall, Saxony, and Sweden. It is found both in the massive state and in the form of acicular crystals, and is composed of Bismuth 81.3, Sulphur 18.7. This is a rare mineral, although its localities are comparatively numerous.

*Bismuth Biende* is a silicate of bismuth which occurs in minute dodecahedral crystals of a dark hair-brown or wax-yellow colour.

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Its general appearance is that of implanted globules, which rarely exceed the size of a pin's head. This mineral, which occurs at Schneeberg in Saxony, is composed of oxide of bismuth, 58.8; silica, 23.8; arsenic acid, 2.2; gangue, 9.1; arsenic, cobalt, copper, and iron, 5.9.

Acicular Bismuth is a sulphide of bismuth, copper, and lead, which occurs in the mine of Klutscheffsky, near Beresof, in Siberia; it is found in acicular crystals of a yellowish-white colour, and contains from 34 to 43 per cent. of bismuth.

Tetradymite is a compound of tellurium and bismuth, and occurs in Sweden and Brazil.

Oxide of Bismuth occurs as a pulverulent coating on some of the other ores of this metal; it is found in Bohemia, Siberia, and at St. Agnes, in Cornwall. It is of a yellowish-green colour, and contains 86 per cent. of that metal.

Carbonate of Bismuth.—This mineral also occurs at St. Agnes, and at Johanngeorgenstadt; it is a straw-coloured compound, with an irregular conchoidal fracture. Its composition has not been satisfactorily determined.

### ESTIMATION OF BISMUTH .- SEPARATION FROM OTHER METALS.

This metal, which for the purpose of analysis must be attacked by nitric acid, is precipitated from its solution in the form of protoxide of bismuth, BiO, which, after being calcined in a small porcelain crucible, and weighed, its equivalent in metallic bismuth is deduced by calculation.<sup>1</sup> This operation must never be attempted in a platinum crucible, as the oxide of bismuth is liable to attack that metal, should any metallic bismuth be liberated through the presence of traces of organic matter. The filter from which the oxide has been detached is burnt in another capsule, treated with a little nitric acid, and strongly ignited for the purpose of decomposing the nitrate of bismuth formed.

When, as is commonly the case, bismuth is found associated with other metals, like itself precipitable by the alkalies and their carbonates, but not by sulphuretted hydrogen, this reagent is employed to effect their separation.

Suphuretted hydrogen is also had recourse to, when the liquor holding in solution the salt of bismuth contains hydrochloric acid, as in this case the precipitate obtained by the carbonated alkalies contains a portion of chloride of bismuth extremely difficult to decompose by any excess of the precipitant.

<sup>1</sup> This oxide contains 89.86 per cent. of metallic bismuth.

#### BISMUTH.

This metal is likewise sometimes precipitated in the form of a black powder, by a bar of iron or zinc introduced into its solution; this precipitate, which is metallic bismuth, is collected on a filter, washed with hot water, and subsequently roasted in a small porcelain crucible. Towards the close of the operation a few drops of nitric acid are added, and the temperature raised for the purpose of decomposing the nitrate of bismuth formed : the bismuth is now weighed in the form of oxide.

Bismuth is separated by a current of suphuretted hydrogen gas from all the metals not converted into sulphides by this reagent. The separation of bismuth from copper is best obtained by the addition of carbonate of ammonia, by which the oxide of copper is retained in solution, whilst the oxide of bismuth is precipitated. After the addition of carbonate of ammonia, the liquor should be allowed to stand for a considerable time in a warm place, as the bismuth is not at once completely deposited. From lead this metal is separated by adding to their solution in nitric acid, sulphuric acid in excess; the liquid is then evaporated until vapours of sulphuric acid begin to be evolved, when the sulphate of bismuth is dissolved in distilled water, and the insoluble sulphate of lead separated by filtration. Bismuth is separated from tin and antimony by treating the recently precipitated sulphide with sulphide of ammonium, containing an excess of sulphur.

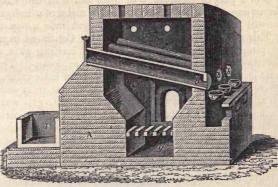
By this means the sulphides of tin and antimony become dissolved, whilst the sulphide of bismuth remains as a precipitate. The separation of bismuth from cadmium has not as yet been satisfactorily effected.

Assay of the Ores of Bismuth.—The assay of the ores of bismuth is conducted precisely like those of the oxidised ores of lead. When the substance operated on contains metallic bismuth, no reducing flux is theoretically required, but as there is, in almost all cases, a portion of oxide present, a little powdered charcoal should invariably be added. On account of the volatility of this metal, it is of importance that a readily fusible slag should be obtained, and for this purpose large quantities, either of carbonate of soda, charcoal and borax, or of borax and black flux, should be employed.

#### METALLURGY OF BISMUTH.

The bismuth of commerce is almost exclusively obtained from the native metal, which is chiefly procured for this purpose from the mines of Schneeberg, in Saxony. The metallurgic treatment of these ores is extremely simple, as it is sufficient to heat them in closed vessels, by which the metal becomes fused, and flows out into proper receivers, whilst the gangue and infusible impurities remain behind.

At Schneeberg, the liquation takes place in cast iron retorts, a b, fig. 168, which are set in an inclined position in a brick furnace, A, provided with a grate at g, for the support of the fuel employed. The minerals treated are sorted by hand, broken into pieces of the size of a hazel-nut, and separated as much as possible from the associated gangue. The charge of each pipe consists of



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about 56lbs. of broken ore, which is introduced at a, and occupies three-fourths of its length, and rather more than one-half its diameter. The sheet iron door is now shut, and when the whole of the tubes in the series have been charged in the same way, the fire is strongly urged: the liquid metal soon begins to flow through the apertures, b, left in the clay plates, by which the lower ends of the tubes are partially closed, and falls into the small earthen pots, c, kept slightly heated by a few pieces of ignited charcoal, introduced into a space left beneath them for that purpose. Whenever it ceases to run freely, an iron rod is inserted through the aperture, b, and the ore is moved about in the retort, in order to remove the obstruction.

The fuel consumed is wood, and each operation usually requires about half an hour for its completion.

As soon as the flow of metal has entirely ceased, the residuum is scooped out with iron rakes, into the water trough, t, and a fresh charge of mineral at once introduced into the pipes. The contents of the pots, c, are, when filled, dipped out with iron ladles, and cast into ingots varying in weight from 25 to 50 lbs.

By this apparatus 20 cwts. of ore are smelted in eight hours, with a consumption of 63 Leipzic cubic feet of wood.

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#### BISMUTH.

The total annual production of this mine amounts to about 10,000 pounds. The bismuth thus directly obtained by liquation is never quite pure, being contaminated by variable quantities of arsenic, iron, and some other metals, from which it is freed by a second fusion with one-tenth of its weight of nitrate of potash.

This metal enters into the composition of some of the best kinds of type, and has the property of imparting to it a clean sharp face. The solder employed in the manufacture of pewter wares consists of 1 part of bismuth, 5 of lead, and 3 of tin. Bismuth also forms one of the ingredients of fusible metal of which, as toys, spoons are made which melt on being put into a cup of hot This alloy is likewise employed on the Continent in making tea. safety plugs for steam boilers, which, by melting at a certain temperature, are intended to prevent their explosion. This contrivance is, however, found in practice to be of little value, as the expansive force causing the explosion is so extremely sudden as not to allow sufficient time for the safety plugs to give way. An alloy composed of 2 parts tin, 3 lead, and 5 bismuth, melts at a temperature of 199° Fahr. This compound is used in making some varieties of stereotype plates, and for various ornamental purposes. A subnitrate of bismuth is used by ladies as a cosmetic. Pearl powder is a similar preparation, obtained by dissolving bismuth in aqua regia, and precipitating by water.

# ANTIMONY.

# Equiv. = 129.3. Density = 6.70.

ANTIMONY is a brilliant metal, of a white colour, slightly inclining to blue. It fuses at a temperature of about 800° Fahr. and contracts but little during congelation.

It is extremely brittle, and possesses a strongly crystalline texture, so that when broken it exhibits beautiful facettes, indications of which may usually be observed on the surface of the cooled ingot. It is slowly but distinctly volatile at a white heat in a closed vessel, but admits of being distilled with tolerable facility in a current of hydrogen gas. When placed on a piece of ignited charcoal and exposed to a stream of oxygen gas, it takes fire and burns with great brilliancy, throwing off its oxide in the form of a yellowish-white smoke, possessed of a peculiar odour somewhat resembling that of arsenic.

Antimony is not sensibly affected by exposure to the air at ordinary temperatures, but is rapidly oxidised when exposed to it in a state of fusion. When fused and strongly heated antimony is allowed to fall on the ground from a certain height, combustion, accompanied by the production of a thick white smoke, immediately takes place. The white smoke is oxide of antimony.

This metal seldom occurs in commerce in a state of purity, but is contaminated with variable quantities of iron, lead, arsenic, and sulphur. To separate these, it may, after being reduced to a fine powder in an iron mortar, be intimately mixed with one-tenth of its weight of nitre, and subsequently fused in an earthen crucible.

By this treatment, the impurities, together with a portion of the antimony, become oxidised, and on breaking the vessel after having allowed it to cool, the antimony is obtained as a metallic button, the surface of which will be covered with a fern-like crystallisation. The purification of this metal may likewise be effected by fusing it when in a finely divided state with a small quantity of its oxide. The fineness of the grain of metallic antimony is regarded as an indication of its purity.

When in a state of fine division, antimony is attacked by hydrochloric acid with the evolution of hydrogen gas, but it has not the

#### ANTIMONY.

property of decomposing water acidulated with sulphuric acid. When attacked by hot concentrated sulphuric acid, it becomes oxidised with evolution of sulphurous acid gas. Nitric acid even when diluted with water, attacks antimony with great facility, and transforms it into an insoluble white precipitate of antimonic acid,  $\text{SbO}_{\delta}$ . Aqua regia readily attacks antimony, and gives rise to the formation of a chloride which is readily soluble in an excess of hydrochloric acid.

Specimens of native antimony have been found in Sweden, France, and Germany.

#### ORES OF ANTIMONY.

Antimony, although occasionally found in a native state, is usually combined with sulphur, and often associated with galena. It also exists in combination with oxygen and arsenic; but the sulphide is the only mineral which can be considered as an ore of antimony.

Native antimony crystallises in forms derived from the rhombohedron, and is often associated with small quantities of iron and silver.

Oxide of Antimony; Antimoine oxydé; Weisspiesglaserz.— This mineral, which is of comparatively rare occurrence, is generally found either in acicular rhombic prisms, or in rectangular plates, having two lateral faces inclined at an angle of 136° 58′. Its colour is either snow-white, pink, or ash-grey. The cleavage is in two directions parallel to the lateral faces of the plates, and is well-defined and readily obtained. The streak is white, and lustre adamantine, shining and pearly. Specific gravity, = 5'56. The analysis of this mineral has afforded to Vauquelin the following results:—

Oxide	of	an	ti	mon	y			86·0
Oxide	of	iro	n					3.0
Silica								
								97.0

According to Berzelius, it is pure oxide of antimony, composed of 84:32 parts of antimony and 15:86 of oxygen. It is extremely fusible, and melts in the flame of a candle.

This substance, which is rare, and consequently of little metallurgic importance, is found in small quantities in veins traversing the primitive rocks, at Przibram, in Bohemia; at Braunsdorf, near Freyberg, in Saxony; at Malaczka, in Hungary; and in some other continental localities. **Sulphide of Antimony;** Antimoine sulfuré; Grauspiesglaserz.— This substance, which is the only mineral sufficiently abundant to be regarded as an ore of antimony, crystallises in forms derived from the right rhombic prism, and is of a lead or steel-grey colour, which is liable to tarnish from exposure.

The cleavage, which is parallel to the shorter diagonal, is highly perfect. The crystals are commonly divergent, columnar, or fibrous. It also occurs in granular amorphous masses. Its specific gravity varies from 4.50 to 4.62; its streak has the same colour as the mineral itself, and on being heated on charcoal before the blowpipe, abundant white fumes and an odour of sulphur are evolved.

This substance, which is commonly associated with iron, zinc, lead, silver, quartz, and sulphate of baryta, occurs in veins traversing various primitive and transition formations. Its most celebrated localities are, Felsobanya, and Schemnitz, in Hungary; Stolberg, in the Hartz; and Auvergne and Dauphiny, in France. Mines of sulphide of antimony have also been worked in different localities in Spain and in the south-western part of the county of Cornwall.

The composition of this mineral is, according to Thomson,-

Antimony Sulphur					
	-			•	100.00

These results indicate that it is a tersulphide corresponding to the formula  $SbS_s$ . The other minerals containing antimony, although rather numerous, do not occur in sufficient abundance to admit of being treated for the metal they afford.

## ESTIMATION OF ANTIMONY-SEPARATION FROM OTHER METALS.

From the difficulty experienced in the preparation of perfectly pure antimonious and antimonic acids, this metal can seldom be determined with sufficient accuracy under these forms, and is therefore more frequently estimated either by difference or weighed in the metallic state.

The precipitation of antimony from its solutions is, in most instances, effected by a currrent of sulphuretted hydrogen gas, a sufficient amount of tartaric acid having been previously added to the liquor to prevent the formation of any turbidity on the addition of distilled water. In some instances in which the presence of tartaric acid would occasion inconvenience in the estimation of the other metals present, hydrochloric acid is made use of for the same purpose; but in this case the results obtained are considered less satisfactory. When the liquor has been properly acidified, a current of sulphuretted hydrogen is passed through it until it acquires a strong odour of that gas, when it is digested at a moderate heat until the liquor again becomes nearly inodorous. The reason for thus expelling the excess of sulphuretted hydrogen is, that sulphide of antimony is slightly soluble in water saturated with that gas, and it consequently follows that unless this precaution were attended to, traces of the metal sought would still remain in solution along with any of the metallic salts not decomposed by this reagent. The precipitate by sulphuretted hydrogen is afterwards collected on an accurately weighed filter, and dried in a water-bath at a temperature of 212° Fahr. When dry, the filter and its contents are again weighed, and on deducting from this the weight of the filter used, the amount of sulphide of antimony will evidently correspond to the difference.

The sulphide of antimony thus obtained is not, however, pure, but invariably contains a greater or less excess of sulphur, which renders it impossible to deduce immediately from it the amount of antimony originally present in the substance analysed.

When it is intended to estimate the metal by difference, the precipitated sulphide is detached as carefully as possible from the filter, and placed in a large flask, into which fuming nitric acid is continuously added, drop by drop, so as to prevent any loss which might occur through the too energetic action of the acid on its contents. More nitric acid is afterwards added, together with a sufficient amount of hydrochloric acid to completely dissolve the whole of the antimony present. If acid of less strength were employed, or aqua regia more or less diluted with water, there would be danger of the formation of a small quantity of sulphuretted hydrogen gas, which, by being evolved into the atmosphere, escapes the oxidising influence to which the other portions are subjected, and vitiates the results obtained. When the precipitate has in this way been entirely dissolved, a solution of chloride of barium is added to the diluted liquor as long as a white precipitate is obtained, and from the weight of the sulphate of baryta formed after it has been properly washed and calcined, is deducted the amount of sulphur present in the sulphide.<sup>1</sup> The weight of antimony is now readily

<sup>1</sup> When a large quantity of tartaric acid has been added to the solution previous to the introduction of the chloride of barium, the sulphate of baryta precipitated will be, to a small extent, contaminated with the tartrate of that base, which cannot be removed even by a protracted washing. This tartrate, during the ignition of the sulphate, becomes converted into carbonate of baryta, and is readily removed by digestion in dilute hydrochloric acid. The residue, on being again washed and calcined, corresponds to the true amount of sulphur contained in the sulphide. obtained by deducting the sulphur thus estimated from the sulphide originally obtained.

When accurate results are required, it is necessary to make due allowance for the quantity of sulphide which remains attached to the filter on which it is collected; and for this purpose it may be either again weighed after its removal, and the calculation made from the quantity actually attacked by nitric acid, or the filter may be burnt, the residue estimated as antimonious acid, and its equivalent in metal added to the results already obtained.

When it is desired to estimate antimony in the metallic form, the sulphide is heated in a current of hydrogen gas, by which sulphuretted hydrogen is formed, and the metal, in a finely-divided state, remains. For this purpose, the precipitated sulphide is introduced either into a small porcelain crucible, having a hole in the cover, through which a glass tube conveying the gas is inserted, or into a bulb blown in a tube of hard glass, connected with an apparatus so arranged as to furnish a current of dry hydrogen. The temperature of the sulphide is afterwards gradually raised, and the current of gas passed until white vapours cease to be produced on presenting at the extremity of the tube a glass rod dipped in liquid ammonia. When the reduction is effected in a porcelain crucible, the action of the current of hydrogen is continued until the substance ceases to lose weight.

To separate antimony from the other metals, advantage is sometimes taken of its insolubility in nitric acid, whilst at others its precipitation by sulphuretted hydrogen, and the solubility of its sulphide in the alkaline sulphides, are the properties of which advantage is taken for this purpose. When an alloy of antimony is attacked by nitric acid, the antimonic acid produced is not quite so insoluble in that menstruum as the peroxide of tin, and distinct traces of oxide of antimony will consequently be retained in solution. This method of separating antimony will, however, be sufficiently exact for technological purposes, and where more accurate results are required, recourse must be had to the abovementioned properties of sulphuretted hydrogen gas and the sulphides of the alkaline metals.

The separation of this substance from the alkaline and earthy metals, as well as from the alkaline earths, is readily effected by passing a current of sulphuretted hydrogen through their solutions, to which an amount of tartaric acid, sufficient to prevent turbidity on dilution with water, has been added.

The excess of sulphuretted hydrogen is subsequently removed by digestion in an imperfectly stopped flask, and the precipitate treated as above described for the determination of the antimony which it contains.

#### ANTIMONY.

To separate antimony from iron, manganese, chromium, nickel, cobalt, and zinc, a current of sulphuretted hydrogen gas is passed through their solutions acidulated with hydrochloric acid. As has been before stated, tartaric acid is frequently employed in order to prevent the precipitation of oxychloride of antimony on the addition of water to solutions of that metal. In the present case, however, the presence of tartaric acid prevents the total precipitation of the associated metals by the ordinary reagents—ammonia, and the alkaline carbonates employed for that purpose ; and therefore, when this acid is employed, it becomes necessary to first saturate the filtrate from sulphide of antimony with ammonia, and afterwards to precipitate them by the addition of sulphide of ammonium.

The separation of this metal from copper, lead, cadmium, and bismuth, is effected by first saturating their solutions in hydrochloric acid, with ammonia, and subsequently adding to supersaturation sulphide of ammonium containing a large excess of sulphur.<sup>1</sup> The beaker containing this mixture is now covered with a glass plate and digested at a temperature of from 90° to 110° for several hours. By this treatment the sulphide of antimony becomes redissolved, whilst the sulphides of the other metals remain in the form of a dense precipitate. This is afterwards separated by filtration from the supernatant liquid, and the sulphide of antimony precipitated from the filtrate by the addition of weak hydrochloric acid. The sulphide of antimony thus obtained is much contaminated by free sulphur, the amount of which must be ascertained by oxidation with strong nitric acid, and separation in the form of sulphate of baryta of the sulphuric acid produced.

From the numerous analogies existing between the compounds of tin and antimony, the separation of these metals from each other is attended with considerable difficulty, and no method by which this can be accurately effected has as yet been discovered. For the purposes of the metallurgic chemist, the following will, however, often prove sufficiently exact. The two metals are dissolved in aqua regia containing an access of hydrochloric acid, and a bar of pure tin is introduced into the solution, properly diluted by distilled water. The liquor is now kept for several hours at a moderate temperature, and the antimony, which will alone be precipitated, is deposited in the form of a dark metallic powder.

### ASSAY OF THE ORES OF ANTIMONY.

From the fusibility of this metal, its ores admit of being reduced at a very moderate heat. For the purpose of assay, the ores of

<sup>1</sup> When the solution contains copper, sulphide of potassium should be employed, as the sulphide of that metal is slightly soluble in sulphide of ammonium.

antimony may be divided into two classes: the first of these comprehends all those compounds in which the metal is combined with either oxygen or chlorine, and in which little or no sulphur is present. The second consists of the native sulphide of antimony, and all other antimonial compounds containing large quantities of sulphur.

1st. All the substances belonging to this division are very readily reduced to the metallic state by being heated at a moderate temperature with finely-divided charcoal, and, when free from earthy or siliceous impurities, their assay may be conducted in an earthen crucible interiorly lined with charcoal, without the addition of any kind of flux.

From the volatility of this metal, it is necessary to avoid the application of too strong a heat; and when the substance examined is contaminated with impurities, the addition of some suitable flux becomes necessary. For this purpose the ore may be intimately mixed either with three parts of black flux or one part of carbonate of soda, and 0.25 of finely-powdered charcoal. In this case the lining of the crucible becomes unnecessary, and after it has remained in the fire until its contents are in a state of tranquil fusion, it should, on being withdrawn, be gently tapped against some hard body, to collect the fused metal in one compact button at the bottom. When the crucible has become cold, it is broken, and the button extracted and weighed. Care is, however, necessary it would otherwise be liable to become broken, and a portion consequently lost.

This method is likewise applicable to substances which, although principally consisting of the oxides of antimony, nevertheless contain small quantities of sulphur; for as the sulphide yields to the black flux just one-half the combined antimony, a very small portion only can be retained in the slags. When oxide of iron is present in the substance treated, this metal is liberated at the same time as the associated antimony, and uniting with it, forms an alloy, by which the result obtained is to a certain degree vitiated.

2nd. The assay of substances belonging to this class may be made either by first roasting the sulphide, and subsequently fusing the oxidised matter with black flux, or by directly fusing the crude mineral with the addition of black flux and finely-divided metallic iron or iron scales. The roasting of sulphide of antimony is, from its great fusibility, and the facility with which it becomes sublimed, an operation requiring much care in its execution; it should consequently be conducted at a very low heat, and the mineral constantly kept stirred with a slight iron rod until all trace of sulphurous acid ceases to be evolved. The residue is then fused with three parts of black flux, and a button of antimony

#### ANTIMONY.

is obtained as in the treatment of the oxidised minerals belonging to the first class.

The antimony contained in the sulphide of that metal is also readily liberated by fusion with metallic iron in a state of fine The sulphide of iron thus produced has, however, so division. very nearly the same density as metallic antimony, that their separation can only be obtained by keeping the contents of the crucible for a considerable time in a state of fusion. When this precaution is taken, two distinct buttons are obtained on breaking the crucible: the one which is at the bottom is of a white colour, and crystallised in white plates, whilst the other is of a bronzevellow tint, and consists of sulphide of iron containing slight traces of antimony. These are carefully detached from each other, and the button of antimony weighed. The long-continued heat necessary to produce this separation has, however, the effect of causing the loss of a considerable amount of antimony by sublimation, which is an inconvenience that cannot be entirely obviated by the most careful manipulation.

In operating in this way, it is also of the greatest importance that the exact amount only of iron necessary to combine with the sulphur present should be added to the pounded sulphide, as from the great tendency of antimony to form an electro-negative element, it would otherwise combine with the excess of that metal, giving rise to an antimonide of iron, one portion of which would contaminate the reduced metal, whilst another would be retained in the slag.

For the reduction of pure sulphide of antimony, 42 per cent. of iron filings is required : these should be free from rust, and in the finest possible state of division, as when larger masses are employed, a considerable amount of antimony is lost in the state of vapour before they can be fully acted on by the surrounding sulphide. Cast iron cannot be employed in the reduction of the sulphide of antimony, as it is not only little acted on by the sulphur, but the slag produced is also found to adhere so firmly to the metal as to be extremely difficult of removal.

If, instead of employing iron and sulphide of antimony alone, a certain proportion of carbonate of soda and charcoal be added to the contents of the crucible, the same results are obtained, and a slag is produced consisting of sulphide of iron and a sulphide of the alkaline base produced.

A good mixture for this purpose consists of 100 parts of sulphide of antimony, 42 of metallic iron, 45 of carbonate of soda, and 5 of finely-powdered charcoal. When thus treated in a lined crucible, and at a moderate temperature, pure sulphide of antimony affords from 65 to 67 per cent. of reduced metal.

Instead of using metallic iron for this purpose, the pure oxide

#### METALLURGY OF ANTIMONY.

of that metal, iron scale, or any ferruginous matter may be employed, provided it be capable of affording, when heated with charcoal and an alkaline flux, a large per-centage of metallic iron. When iron scales are employed, they should be added to the sulphide of antimony in the proportion of 40 parts of the former to 100 of the latter; and this, with the addition of 100 parts of carbonate of soda, and 15 of charcoal, will, with careful firing, afford a produce of from 65 to 67 per cent. of reguline antimony.

Mr. Mitchell states that the best method of assaying sulphide of antimony consists in mixing it intimately with four parts of cyanide of potassium, and heating very gently in an earthen crucible. The heat required in this case is so extremely low, that little if any of the metal is lost by sublimation; whilst by all the other processes, a notable quantity, often amounting to 5 or 6 per cent., is in this way driven off. It is, therefore, evident that the estimation of antimony by the dry way should rather be considered as a commercial approximation than as being rigorously exact; and when pure sulphide is the substance operated on, its examination will prove of but little value, as every 100 parts of that compound correspond to 72.8 of metallic antimony.

When more rigorously exact results are required, recourse must be had to humid analysis. For this purpose a weighed portion of the sulphide to be examined should be boiled with aqua regia until the whole of the soluble matters are dissolved. The residue, which consists of gangue and undecomposed sulphur, is now separated by filtration, dried, ignited, and weighed. Tartaric acid is then added to the filtrate to prevent the precipitation of any oxychloride on dilution with water, and the antimony is precipitated in the state of sulphide by a current of sulphuretted hydrogen. The amount of metal in this precipitate is determined by one of the methods already described, whilst the amount of sulphur originally present in the ore is readily found by first ascertaining the loss sustained by the dry gangue during ignition, and subsequently precipitating the oxidised sulphur existing in the filtrate in the form of sulphuric acid by the addition of chloride of barium. On ascertaining the amount of sulphur corresponding to the sulphate of baryta thus obtained, and adding it to that directly estimated by difference, the whole amount combined with the antimony is obtained. The other metals and earths are, when necessary, separated by the ordinary routine of chemical analysis.

#### METALLURGY OF ANTIMONY.

From the fusibility of sulphide of antimony, its separation from the siliceous and earthy gangue with which it is associated

#### ANTIMONY.

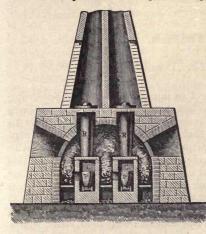
is readily effected by a simple liquation conducted at a very moderate heat. On the continent, this operation is carried on in vertical retorts in a way shortly to be described; but in this country a reverberatory furnace of peculiar construction is employed. The hearth of the apparatus is composed of a mixture of sand and clay, solidly beaten together, and sloping rapidly in all directions towards the centre, where, at the lowest part of the basin thus formed, is situated the tap-hole for the escape of the different liquid products. When the mineral operated on is tolerably free from earthy or other impurities, the operation of liquation may frequently be dispensed with, but with the poorer varieties of ore it becomes indispensably necessary. In this case the impure sulphide is charged on the floor of the furnace, and in proportion as the temperature begins to be elevated it becomes liquefied, and escaping through the tap-hole in the bottom of the hearth is received in a basin prepared for that purpose on the outside of the brick-work of which the furnace is constructed.

To obtain metallic antimony, the sulphide is carefully roasted in a reverberatory furnace until the whole of the sulphur is expelled, and a grey oxide alone remains. This oxide is afterwards mixed with one-tenth of its weight of crude tartar, and reduced in large earthen crucibles heated in a wind furnace. The metal obtained by this process is, with the exception of a certain admixture of iron, tolerably pure, and is at once ready for the market. Instead of thus expelling the sulphur by roasting, and subsequently reducing the oxide formed, the reduction of the sulphide is often directly effected by fusion with metallic iron in a reverberatory furnace furnished with a concave hearth.

According to Berthier, an excellent product of metallic antimony is obtained from a mixture of 100 parts of purified sulphide, 60 of iron scales from the hammer or rolling mill, from 45 to 50 of carbonate of lime, and 10 to 12 of powdered charcoal. From these proportions, a yield of nearly 70 per cent. of antimony is readily procured. The antimony obtained by this process is not, however, sufficiently pure for many commercial purposes, as it contains large quantities of iron and other substances, which are separated by a second fusion in large earthen crucibles with a mixture of antimonic acid.

In works where antimonial ores are smelted by means of crude bitartrate of potash, the scoriæ which cover the surface of the metal are not thrown away, as they retain a certain proportion of antimony in combination, from which a secondary product constituting a coarse kind of Kermes Mineral is obtained. These slags consist of sulphide of potassium and antimoniate of potash, and, on being treated with water, undergo a decomposition by which the kermes is precipitated : this, under the name of kermes by the dry way, is sold as a veterinary medicine.

At Malbosc, in the department of Ardèche in France, the separation of the sulphide of antimony from its associated gangue is effected by means of a peculiar apparatus, of which fig. 169



represents a vertical section. For this purpose the mineral is placed in large retorts, R, of which four are set in each furnace. An aperture is left at the bottom of each of these cylinders, which corresponds with a similar opening by which they are supported. Beneath these, in separate chambers, c, are situated the earthen pots, P, in which is received the melted sulphide in proportion as it descends from the cylinders above.

The fuel consumed on the grate consists of fir wood, and the sulphide obtained is converted into metallic antimony by roasting in a reverberatory furnace, and subsequent reduction by a mixture of 20 per cent. of pulverised charcoal, which has been saturated with a strong solution of carbonate of soda.

The brittleness of this metal prevents its being extensively employed in a pure state, but its alloys, which are very numerous, are much used. The most important of these is type metal, which consists of 6 parts of lead and 2 of antimony; common stereotype metal is composed of 6 of antimony and 1 of lead. Britannia metal is also a compound of the same class, containing variable quantities of copper, tin, bismuth, and antimony. Antimony, in the form of a soluble tartrate of antimony and potash, is the tartar emetic of the apothecary; and antimony, with a mixture of lead, forms the alloy on which music is engraved.

# ARSENIC.

# Equiv. = 75. Density = 5.88.

ARSENIC is a brittle metal, of an iron-grey colour, and possessing a strong metallic lustre. When heated to 356° Fahr. it sublimes without first entering into fusion, and at the same time emits an odour strongly resembling that of garlic. In close vessels it may be sublimed without change; but, if air be admitted, it is rapidly converted into a white oxide. According to Hahnemann, this metal is slowly oxidised and dissolved by being boiled in distilled water. When exposed to air and moisture, it generally acquires on its surface a dark film, which is extremely superficial; but it has been observed by Berzelius, that some specimens may be kept in open vessels for several years without losing their lustre, whilst others are in a short time oxidised throughout their whole substance, and fall into powder. This difference has been recently accounted for by supposing it to arise from the presence of potassium derived from the black flux employed in its preparation. The metal obtained by the sublimation of commercial cake arsenic is not subject to this oxidation by exposure to the atmosphere. The product of this spontaneous change appears to be a mixture of oxide and metallic arsenic, and is known on the Continent under the name of fly-powder.

Arsenic is a highly combustible body, and burns with a bluishwhite flame and the formation of arsenious acid,  $AsO_3$ . This oxide, which is generally known by the name of white arsenic, is the most common preparation of this body. It is obtained by roasting in a reverberatory furnace the more common ores of arsenic. The arsenic of commerce is procured during the treatment of mispickel, the arsenical ores of tin, arsenical minerals of cobalt, and some of the ores of copper, containing this body in conjunction with sulphur.

The determination of arsenic, when existing in the form of arsenious and arsenic acid, is variously effected according to the nature of the other bodies contained in the solution. If, in addition to arsenic acid, the liquor only contains nitric acid, without any traces of other fixed matter, it is mixed with a weighed quantity of pure oxide of lead which has been previously heated to redness in a porcelain crucible. The solution is now evaporated to dryness, and the residue ignited and weighed. The quantity of arsenic acid originally present is obtained by deducting from the weight of the ignited residue that of the oxide of lead added at the commencement of the operation. In order that this process should succeed, it is of course necessary that no other acid be present which, by uniting with the oxide of lead, is capable of forming a compound not decomposed at a red heat: the presence of ammonia is equally detrimental to the accuracy of this method of estimation. The separation of arsenic from other bodies is effected by the same means as are employed to eliminate antimony from solutions containing other metals; but, from the similarity in the behaviour of these substances when treated by the different reagents, great difficulty is experienced in separating them from each other. This difficulty is still further increased when tin is also present.<sup>1</sup>

Arsenious acid, when treated with charcoal, becomes reduced to the metallic state. The metallic arsenic of commerce is prepared by decomposing, by the aid of heat, the mineral called mispickel, as also from the other ores containing arsenic in combination with iron and sulphur. For this purpose the pounded ore is placed in earthen retorts 4 ft. 6 in. in length, and about a foot in diameter, in which some pieces of old iron are introduced, with a view to more effectually retaining the combined sulphur. Receivers are now adapted to the different retorts, which are moderately heated by a fire placed beneath them; the mineral is thus decomposed into sulphide of iron, which remains in the retort, and into metallic arsenic, which is sublimed and condensed in the receivers. The arsenic obtained in this way is purified by second distillation with a small quantity of powdered charcoal.

Arsenic is used in small quantities in the preparation of various alloys, and particularly in the manufacture of shot. When mixed with lead in the proportion of about one per cent., it is found not only to impart to it a certain degree of hardness, which is advantageous, but it likewise gives to it a tendency to form into regular globules, which much facilitates the manufacture.

Arsenious acid, the white arsenic of commerce, is prepared by roasting certain arsenical ores, such as those of iron, nickel, and cobalt, as also from the arsenical fumes condensed in the flues leading from furnaces in which the roasting of tin

<sup>1</sup> For the best method of separating these metals, see Fresenius, Quantitative Analysis, § 130, p. 345.

ores is conducted. The substance from which the arsenious acid is to be prepared is usually heated on the sole of a reverberatory furnace, through which a current of air, after passing through the grate, is allowed to play. By this treatment the sulphur is converted into sulphurous acid, which escapes through the chimney whilst the arsenious acid at the same time produced is condensed in proper chambers placed in the flues for that purpose. To obtain pure arsenious acid, the tirst products thus directly procured by sublimation are subjected to a second treatment in cast iron tubes provided with wrought iron receivers. Freshly-prepared arsenious acid assumes the appearance of a perfectly transparent solid mass, but by exposure it becomes transformed into an opaque body resembling porcelain.

Arsenious acid is largely employed to give a peculiar porcelainlike hue to glassware. It is likewise extensively used in the preparation of various pigments, among which may be mentioned orpiment, or *king's yellow*, and realgar, which is another sulphide of a fine red colour. Arsenious acid is also extensively employed in the manufacture of emerald green—an aceto-arsenite of copper much used by paper-stainers.

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# Equiv. = 100.07. Density = 13.568.

MERCURY, or Quicksilver, differs from all the other metals in being liquid at ordinary temperatures. It has a silver-white colour, with a strong metallic lustre, and is not, if quite pure, tarnished by exposure in the cold to a moist atmosphere. If, however, it contains traces of other metals, the amalgam is rapidly oxidised, and the surface of the bath quickly covered by a grey-coloured powder. This metal is solid at a temperature of 39° or 40° below zero, and is then both ductile and malleable. In polar latitudes the cold is sometimes so intense as to cause the congelation of mercury, but a similar result may be obtained by a freezing mixture composed of ether and solid carbonic acid. The same effect is also produced by a mixture of pounded ice and crystallised chloride of calcium. If a rather large quantity of mercury be operated on, and, after being placed in a platinum crucible, it be gradually exposed to a proper refrigerating mixture, distinct octahedral crystals are readily obtained. The mercury in this case becomes congealed around the sides of the vessel; and, in pouring out the portion which still retains its liquidity, brilliant crystals belonging to the cubic system are found coating its sides. Considerable contraction is likewise observed to take place at the moment of congelation; for while its density at 47° is 13.545, that of frozen mercury amounts to 15.612.

Mercury is sometimes adulterated with lead and bismuth; but such impurities may be readily detected, both by the want of fluidity of the mixture, and also from its leaving a residuum when sublimed in an iron spoon. The tension of mercurial vapour is sensible at ordinary temperatures, although, from being extremely feeble, it cannot be estimated with a great degree of precision. That mercury is volatile at common temperatures is readily perceived by suspending a sheet of gold leaf in the upper part of a bottle in the bottom of which a little of this metal has been placed. On removing this arrangement to a cool place, and allowing it to

remain a few days without being disturbed, that part of the gold which is nearest to the surface of the mercury will be found to have become whitened by its vapour, whilst that portion of the sheet which is in the highest part of the bottle remains unaltered, as, from the feeble volatility of this metal at ordinary temperatures, its vapour merely forms an extremely thin stratum immediately over the surface of the metallic bath.

The mercury of commerce, when it comes directly from the mine, is in most instances nearly pure, but is sometimes contaminated by dissolving small quantities of other metals, and almost invariably contains a greater or less amount of oxide, which becomes disseminated throughout the mass. With a view to the separation of these impurities, mercury is frequently distilled from an iron retort, and again condensed in a vessel containing cold water. For this purpose one of the wrought iron bottles in which quicksilver is imported may be conveniently employed. One of these, after being about half filled with the metal, should have attached to it a piece of iron gas-pipe bent nearly at right angles, and furnished at its open extremity with a tube formed of several layers of linen or cotton cloth, and of which the end is made to plunge into a basin containing cold water. The open extremity of the iron pipe, together with the piece of linen hose attached, are moistened by a constant stream of cold water, which is made to flow upon it through a small stop-cock, and the iron bottle is heated in a furnace until the vapour of mercury begins to be plentifully given off. The ebullition of the metal is often attended with violent explosions, and care must be taken so to regulate the heat as to prevent the projection of any part of the charge through the iron tube into the receiver. By operating in this way, the greater portion of the foreign metals are retained in the retort, whilst the mercury passes over in a purified state into the vessel containing the cold water. A certain portion of the impurities is, however, by this process carried over into the receiver; and consequently, when an absolutely pure specimen is required, their separation should be effected by some other means. The best method of doing this is to treat the mercury to be purified with common nitric acid diluted with about twice its volume of distilled water. The whole is then heated to about 110° Fahr., and nitrate of protoxide of mercury will be rapidly This nitrate and the free acid react on the foreign formed. metals present, which are held in solution in the form of Any oxide of mercury originally present is also dissolved salts. by the nitric acid with formation of a nitrate. The action is continued during twenty-four hours, and the mixture occasionally agitated.

Lastly, the water is separated by evaporation; and the nitrate which remains in the form of a crystalline crust on the surface of the metal, is removed. The metallic mercury is now separated, and, after being washed with distilled water, is first dried with bibulous paper, and subsequently by exposure under a bell-glass to the desiccating influence of caustic lime.

When mercury is merely soiled by a slight admixture of oxide, it is readily removed by brisk agitation in a glass bottle with a small quantity of strong sulphuric acid. By this treatment the metal is divided into extremely small globules, which expose a large surface to the action of the acid. At the expiration of from three to four days the acid may be poured off, and the purified mercury washed and dried.

Mercury is not attacked by strong hydrochloric acid, even when its action is aided by ebullition. Dilute sulphuric acid likewise fails to dissolve it; but if concentrated acid be employed, it is, with the aid of heat, rapidly converted into sulphate of mercury, and gives off an abundant supply of sulphurous acid gas. Nitric acid attacks this metal with great energy even in the cold; and, when moderately diluted with water, binoxide of nitrogen is plentifully evolved.

Mercury combines with great readiness with certain other metals, such as gold, silver, zinc, tin, lead, and bismuth, and forms, when in suitable proportions, solutions of those metals. These mercurial alloys are called amalgams, and this property of the metal is extensively employed in extracting gold and silver from their ores, as well as in gilding, plating, and the manufacture of looking-glasses. Mercury is besides the basis of many powerful and valuable medicines, and is, on account of its great density, and the regularity of its expansion and contraction under the influence of increased and diminished temperature, preferred to all other liquids for filling the tubes of thermometers and barometers. This metal is likewise employed for anatomical injections, and, when united with tin and zinc, forms the best exciter which can be applied to the rubbers of electrical machines. Nitrate of mercury is employed as a wash for rabbit and hareskins, and gives to their furs the property of felting, which they do not naturally possess.

#### ORES OF MERCURY.

Native Quicksilver; Mercure natif; Quecksilber, in fluid globules, disseminated through the gangue, occurs in most of the mines producing the different mercurial ores. It is usually much

disseminated in the rock, but is sometimes so accumulated in cavities as to admit of being readily dipped up.

**Sulphide of Mercury**; *Mercure sulfuré*; *Zinnober.*—This substance crystallises in rhombohedral prisms, but most commonly occurs in an amorphous state. Sulphide of mercury is, properly speaking, the only ore of that metal, and is distinguished by its dull red colour and bright scarlet streak. Its lustre is, when amorphous, unmetallic; but when crystallised, adamantine. It is readily sectile, and in most instances nearly opaque.

Two specimens of this mineral, analysed by Klaproth and Lebererz, yielded the following results :---

			From Japa sed by Kla		From Idria, analysed by Lebererz.			
Mercury		•	84.50	•		51.80		
Sulphur			14.75			8.20		
Bituminous	ma	$\operatorname{tter}$			•	6.80		
Gangue					•	32.00		
Water	•	•		•	•	3.20		
			99.25			102.00		

It follows that this substance, when pure, consists of one atom of mercury united to one of sulphur; and its composition is, therefore, expressed by the formula HgS. Cinnabar mostly occurs in connection with talcose and argillaceous shale, or in some other stratified deposit. From the volatility of this mineral it is not found in large quantities in crystalline or igneous rocks, although small specimens have sometimes been observed disseminated in granite. When the ores of mercury are met with in stratified rocks, they are usually found in the form of veins or lodes; but when, as is sometimes the case, the matrix is sandstone, they are commonly disseminated in minute grains throughout the mass.

The principal mines from which mercury is extracted are at Idria in Austria, Almaden in Spain, in California, in the Palatinate, on the Rhine, and in various places in Peru. Mines of this metal have also been worked in Mexico, Hungary, Sweden, China, and Japan, as well as at Arqueros in Chili.

At Îdria the sulphide of mercury is worked in a formation chiefly composed of a compact black limestone associated with an argillaceous schist, with which it is so intimately mixed as to appear to have been formed contemporaneously with it. The mines of Idria were discovered in the year 1497. The workings are carried on by means of small galleries, as the rock is too friable to admit of larger excavations. The ore, which is prin-

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cipally bituminous cinnabar, associated with native mercury, is obtained at a depth of 850 feet from the surface. The yearly production of this mine might, according to Dr. Ure, be easily raised to 600 British tons; but, with a view to maintaining the price of mercury, the Austrian government has restricted its annual yield to one-fourth of that sum. In the year 1803, a most disastrous fire occurred in these workings, which, from the quantity of mercury sublimed, affected more than 900 persons in the neighbourhood of the mines with nervous tremblings and other diseases; and, in order to extinguish the smouldering galleries, it was found necessary to inundate the mine. In some places native mercury is so abundantly disseminated among the ore and bituminous schist that, when the ground is first broken, it escapes in the form of large globules, which run down and collect in considerable quantities in the bottoms of the levels. The pure mercury is first separated by filtration from the earthy matters, which are afterwards mechanically treated previous to their reduction in furnaces prepared for that purpose.

From the mines of Almaden, which are situated near the frontier of Estremadura, in the province of La Mancha, the Greeks are said to have imported cinnabar at least 700 years before the Christian Era, and Pliny states that in his time 100,000 lbs. were annually obtained from the same locality. The vein, which varies from 14 to 16 yards in thickness, extends from the town of Chillon to Almadenejos, and a black slate, plentifully impregnated with metallic mercury, is mined near the rivulet Balde Azogues.

The mines, which do not exceed 300 yards in depth, are excavated in argillaceous schist, and sandstone-grit deposited in horizontal beds, which have been sometimes intersected by eruptions of granite and black porphyry. The ore thus extracted yields by metallurgic treatment on an average 10 per cent. of metal, although it is shown by analysis that considerable loss is experienced during the operation. These mines annually afford large quantities of mercury.

Near these celebrated workings lie those of Las Cuebas and Almadenejos, which, although of much smaller extent, still produce considerable weights of mercury. The mines of this district, after having been known from remote antiquity, became the property of the religious knights of Calatrava, who had assisted in driving out the Moors from Spain, and who farmed off these deposits to the celebrated Fugger merchants of Augsbourg. Since the year 1645 they have been explored on account of the government.

The mines of the Palatinate, although of less extent than the above, are nevertheless of sufficient importance to merit the atten-

tion of the government, by which they are farmed out to private speculators. These workings, which are numerous, and situated in various geological positions, are seldom prosecuted at any very considerable depth from the surface. Among the most remarkable are those of Drey-Koenigszug, at Potzberg near Kussel. These are sunk to a depth of above 220 yards, and annually produce about 30 tons of mercury. The mineral is a fine sandstone, strongly impregnated with cinnabar.

The mines of Hungary, Bohemia, and the other parts of Germany, are estimated to yield collectively an annual supply of from 35 to 40 tons.

The mines of Guancavelica in Peru, have likewise afforded a large amount of mercury, and are particularly interesting, from the circumstance of the quicksilver being directly employed in treating the ores of gold and silver, which are so abundantly furnished in that part of America.

The South American miners had recourse, in 1782, to the mercury extracted in the province of Yun-nan in China, where the separation of the metal is effected by placing the ore in pits or wells, previously heated by a fire of brushwood. On cooling, the quicksilver becomes condensed, and is then collected from reservoirs, where it is deposited in a liquid state.

The other minerals containing mercury are of but little commercial importance. Chloride of mercury, or horn quicksilver, is a mineral of a greyish-white or yellow colour, and conchoidal fracture. It is chiefly found at Almaden in Spain, and at Moschellandsberg in the Palatinate, where it covers the surface of a ferruginous gangue, and sometimes affords distinct and well-defined crystal, belonging to the right prismatic system. Specimens of this mineral are also sometimes obtained at Idria, and at the mine of Horzowitz in Bohemia.

An iodide of mercury is found in some of the Mexican mines; its colour is nearly similar to that of cinnabar, but of a somewhat deeper tint. This mineral, which was discovered by M. del Rio, has not as yet been fully examined.

Native amalgam, a natural alloy of mercury and silver, will be described when treating of the latter metal.

#### ESTIMATION OF MERCURY .--- SEPARATION FROM OTHER METALS.

This metal is either directly estimated in the metallic state, or in the form of chloride, Hg<sub>2</sub>Cl, commonly known as calomel. When it is required to separate with great accuracy metallic mercury from the substances with which it may be associated, the following method can be conveniently employed. A long tube of hard glass, a b, of the same diameter as that employed for making organic analyses, is drawn out by one of its extremities, in the way shown in fig. 170, and in this part a bulb, B, is so blown as to be between two parts of the narrowed tubing. The contraction at a is now



slightly plugged with a bit of asbestos, so as to allow of a free circulation of gas, whilst it prevents any solid matter from

being drawn into the smaller elongation between a and B.

Powdered quick-lime is afterwards introduced into the tube, and slightly tightened with a piece of the glass rod, care being at the same time taken that the aperture be not hermetically closed ; the mercurial product to be examined is then introduced at c, and its weight accurately noted. When the substance has thus been deposited in the situation above indicated, the remainder of the tube is filled with quick-lime, and its end closed with a perforated cork, into which a piece of small glass tubing is accurately fitted. The prepared tube is now placed in an ordinary combustion furnace, and a current of dry hydrogen gas introduced by the extremity, b. The part of the tube between b and c is first warmed, and the heat progressively advanced in the direction of a. The mercurial product is by this treatment decomposed, and the volatile metal being carried forwards by the current of hydrogen gas, is condensed and collected in the bulb, B, prepared for that purpose. A small quantity of watery vapour is also generally condensed at the same time, but by a continued evolution of dry hydrogen gas this is ultimately carried off in the form of vapour. At the close of the experiment, when the whole of the mercury has been condensed, and the watery vapour has all passed off, the tube on either side of the bulb, B, is cut with a sharp file, and the bulb itself accurately weighed with the mercury it contains. The metal is then poured out, and, for the sake of accuracy, any portions which may still adhere to the glass are removed by washing, first with a little nitric acid, and subsequently with distilled water. After being thoroughly dried, the bulb is again weighed, and on subtracting the weight of the empty glass from the result first obtained, the quantity of reduced mercury is at once ascertained. In conducting this experiment, it is of importance that a large quantity of moisture should not be contained in the substance operated on, as by its condensation in the bulb, and subsequent evaporation, a sensible amount of mercury is frequently carried off. If the mercurial product should in any form contain nitric acid, copper turnings must be substituted for lime in the com-

bustion tube, in order to decompose the nitrous vapours which would otherwise attack the mercury collected in the bulb, B.

When soluble mercurial products are to be examined, this metal, together with all the others present, which are precipitated by sulphuretted hydrogen, are thrown down in the form of sulphides by that reagent, and afterwards treated with quick-lime and dry hydrogen gas, in the way above described. The sulphide of mercury is decomposed, and the metal collected in the receiver, B, whilst the non-volatile bodies are retained in the combustion tube.

Instead of separating the mercury from its solution by sulphuretted hydrogen, protochloride of tin, or a bar of metallic iron, is occasionally employed; but even in this case, if accurate results are to be obtained, it is necessary to distil the precipitate in the apparatus, fig. 170.

When protochloride of tin is thus used, the mercurial solution should be first rendered acid with hydrochloric acid, and a solution of the chloride added, in which hydrochloric acid had been previously poured, until it had been rendered perfectly limpid. This precaution obviates the necessity for filtration, which would otherwise have been indispensable. When this reagent is added in proper amounts, the whole should be heated to ebullition, care being taken that the boiling be not too long continued, as in that case there would be some danger of a loss of mercury, arising from sublimation. The mouth of the flask in which the precipitation has been effected is now closed, and on cooling, the mercury is deposited in the form of a black powder, which, on being boiled with a little weak hydrochloric acid, becomes united in one globule, from which the liquor is readily decanted off. This may be washed with hot water, and subsequently weighed in a small porcelain capsule; but where great accuracy is required it is far better to dry the black powder at first precipitated, and afterwards subject it to the combined action of heat and hydrogen gas, in the apparatus above described.

The precipitation by a bar of iron is to be avoided in all cases where other reagents can be obtained, and in this case a subsequent distillation in an atmosphere of hydrogen gas becomes almost indispensable.

Assay of the Ores of Mercury.—All minerals containing mercury, whether in the metallic state, or as oxide, sulphide, selenide, chloride, or iodide, admit, after being reduced to a fine powder, of being assayed with considerable accuracy, by distillation with quick-lime, in an atmosphere of hydrogen gas; but when cinnabar is the compound operated on, it may sometimes be distilled without change by being strongly heated, without the addition of any reagent, in a hard glass retort. From the sublimed

sulphide, which is collected and weighed, the per-centage of metallic mercury is readily deduced, as every 100 parts of the former is found to correspond to 86 parts of the latter. The ores containing sulphide of mercury are, however, not unfrequently associated with carbonate of lime and bituminous matter, and it therefore often happens that a little metallic mercury is liberated during the distillation. This, it is evident, would vitiate the results obtained, in proportion as the quantity is more or less considerable. When metallic mercury has been in this way liberated, the mixture of the reduced metal and cinnabar is first weighed in the state in which it has been deposited, and subsequently treated with dilute nitric acid, by which the free metal is dissolved, whilst the sulphide remains intact. The weight of this is now taken, and from it the amount of dissolved mercury is ascertained by difference. To this is added the weight of sulphur necessary to convert the whole into cinnabar, which, added to the amount of sulphide actually found, gives the per-centage of cinnabar originally contained in the mineral examined.

This method of estimating the value of ores containing sulphide of mercury, is, however, much less accurate than distillation with lime in a current of hydrogen gas, and the results obtained should therefore be regarded as being no more than an approximation, which may in some cases be of value, when the means of conducting a more careful experiment are not readily to be procured.

### METALLURGY OF MERCURY.—TREATMENT OF MERCUBIAL ORES AT IDBIA.

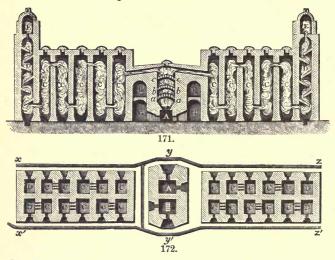
The ores treated are here divided into two classes : the mineral in lumps varying from the size of a nut to a cubic foot, and those fragments of which the size ranges from that of a nut to the finest dust.

The first class comprises three subdivisions; namely, the poorest species, affording only one per cent. of mercury; the massive sulphide, consisting of the richest selected fragments, often containing 80 per cent. of metal; and, lastly, the splinters arising from the picking and sorting of the different ores, and which yield from 1 up to 40 per cent.

The second class is also subdivided into three varieties, and comprises the fragments extracted from the mine in small pieces, and which on an average afford from 10 to 12 per cent. of metallic mercury; bits of ore separated by washing on a sieve, and containing 32 per cent. of metal; and, lastly, the fine sand and paste called *schlich*, obtained by stamping and washing the poorer ores: this generally affords a produce a little superior to 8 per cent.

The metallurgic treatment of these several products consists in subjecting them to a process of roasting in a large distillatory apparatus, in which the sulphur is converted into sulphurous acid, whilst the metallic mercury is set free and condensed in a series of large chambers arranged on either side of the furnace for that purpose.

This apparatus consists of a large roasting kiln,  $\Lambda$ , figs. 171 and 172, furnished on either side with a series of chambers, c, in which the mercurial vapours are condensed.



The larger fragments of the mineral treated are closely piled on the hollow arch, a a, until the space between it and the next has been entirely filled with it. On the second perforated arch, b b, are placed, in shallow earthenware pipkins, the fragments of smaller dimensions, and on the third, c c, are deposited, also in earthen vessels, the slimes arising from the mechanical treatment of the poorer ores.

When the furnace has been thus charged, the fire is lighted on the grate, and the heat progressively raised until the decomposition of the mineral begins to take place. The sulphide of mercury, placed in immediate contact with a current of heated and strongly oxidising air, which enters the furnace through apertures opening into the spaces, G, H, is sublimed and rapidly decomposed, whilst the metallic products are conducted by proper channels into the condensing chambers, c. The greater portion of the mercury becomes condensed in the three first chambers, and is conducted by the gutters x y z, x' y' z' into a covered reservoir, prepared for its reception beneath the level of the floor. In the last chamber of the series, a considerable amount of water, and but very little mercury, is condensed. These products are, on account of the impurities which they contain, carried off by a separate set of gutters, to a tank, in which they are allowed to accumulate. The mercurial dust which contaminates the metalobtained from these latter chambers is subsequently separated by filtration, and mixed with some of the finer ores, to be again treated in the furnace.

In order effectually to condense the last trace of mercury passing through the apparatus, a stream of cold water is constantly made to flow through the chambers, D, on inclined tables, extending nearly from one wall to the other of the building, and between these the vapour and gases are obliged to circulate before escaping through E into the atmosphere.

The mercury is afterwards filtered through thick linen bags, to separate the solid impurities, and subsequently packed in wrought iron bottles for exportation.

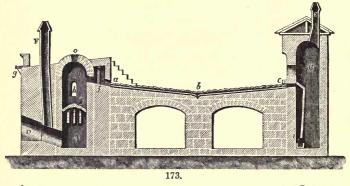
This arrangement, which is perhaps the largest metallurgic erection in the world, is charged in three hours by the united labour of 40 men. The wood employed as fuel is usually beech, and the distillation lasts from 10 to 12 hours, during which time the whole furnace is kept at a cherry-red heat. A complete charge for the double apparatus is from 1000 to 1200 quintals of ore, which produce from 80 to 90 quintals of metallic mercury. The furnace requires, according to the season of the year, from five to six days to cool, and therefore, when the time necessary for charging and withdrawing the residue is included, but one distillation can be made in the course of a week. This furnace is 180 feet long, and 30 feet in height; it was first erected at Idria, in the year 1794, before which time an aludelle furnace, similar to that now to be described, was employed.

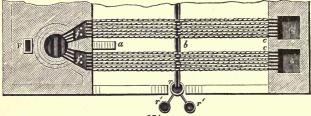
In the year 1812, the mines of Idria yielded 56,686 quintals of mechanically prepared ore, which afforded 4,832 quintals, or about  $8\frac{1}{2}$  per cent. of metallic mercury.

#### ALUDELLE FURNACE OF ALMADEN.

This apparatus is represented in figs. 173 and 174, of which the first is a vertical section, and the second a sectional plan. These furnaces, which are called in the country *buytrones*, consist of a circular chamber, A B, separated into two compartments by a brick arch, k, pierced with numerous apertures. The mineral is piled in the space, B, above the arched diaphragm, the larger masses being

placed first, and the smaller fragments afterwards. The top is then covered with soft bricks, formed of clay, kneaded with fine schlich. At the upper extremity of the cavity, B, is arranged a system of openings, f, which communicate with a series of earthen adapters, fitted into each other, and resting on the doubly inclined surface of the terrace,  $a \ b \ c$ . These earthen pipes or *aludelles*, fig. 175, are merely





174.

thrust into one another, and luted with a little softened loam, by which the leakage of the joint is partially obviated. The condensed mercury partly

remains in the aludelles, but another and larger portion flows through a hole pierced in the aludelle placed at the low-



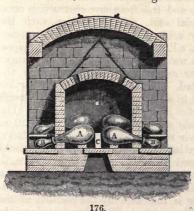
est part of the series, and is collected in the gutter, b, by which it is conducted through wooden spouts into the receiving basins, r r'. The uncondensed gases, mixed with the mercurial vapours, pass through the apertures, c c, into the chambers, c, where, passing under a diaphragm, e, a certain portion of metal is deposited in a vessel i, filled with water. What still remains passes into the upper part of the chamber, from whence it escapes into the atmosphere through a small chimney, E. The mercurial soot which accumulates on the sides of this chamber is occasionally swept down, and after being kneaded into bricks with the addition of softened clay, is again treated in a subsequent operation.

The fuel employed is brushwood, which being ignited in the space, A, beneath the arched diaphragm, affords the amount of heat necessary for the proper working of the furnace. The aludelles are placed in 12 ranges of 25 in each set; the fuel is introduced through the opening, D, and the smoke and other products of combustion are carried off by the chimney, F. *a* are the steps for mounting on the top of the furnace, and *g* a small gutter by which the rain water is carried off. The mineral is introduced into the furnace through the door, *h*, and opening, *o*, which are afterwards securely luted up.

The firing is continued during 12 or 13 hours, and the apparatus is then allowed to cool during 3 or 4 days; at the expiration of which time it is cleaned out, and again charged for another operation.

# GALLERY OF THE PALATINATE. — APPARATUS EMPLOYED AT LANDSBERG.

In the Duchy of Deux-Ponts, where considerable quantities of mercury are extracted, a peculiar apparatus called a gallery is employed. The mineral here treated consists of a mixture of sulphide of mercury and carbonate of lime, which is heated in a kind of earthen retort, or *cucurbit*, of which several are arranged in one furnace, as shown in fig. 176. The number of cucurbits,

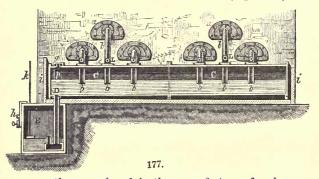


A, contained in one gallery varies from 30 to 52, and to each of these is adapted a stoneware receiver, B, partially filled with cold water. Into each of the retorts are introduced from 56 to 70 lbs. of cinnabar, and from 15 to 18 lbs. of quick-lime, a mixture which should fill about two-thirds of its capacity.

The sulphide of mercury is in this case decomposed by the lime; sulphide of calcium and sulphate of lime are formed, and the

liberated metal is condensed in the stoneware bottles. The fuel employed, which is pit coal, is burnt on a grate which is situated at c. The dome is perforated with openings for the purpose of creating a draught.

To obviate the inconvenience and loss experienced by the older methods of distilling mercury, an apparatus was erected, in 1847, at Landsberg, near Obermoschel, in the Bavarian Rhein-kreis. This arrangement consists of a series of retorts of the form indicated at a, fig. 177. These are set in masonry, precisely in the



same way as those employed in the manufacture of coal gas, and are fitted at one end with an eduction tube, b, and at the other with an air-tight stopper, kept in its place by an iron screw. The eduction pipes are each furnished with a nozzle, L, closed by a screw plug, through which a wire may be introduced, to ascertain that the tube is clean, and free from any obstruction occasioned by adhering mercurial soot. In connection with the pipes, b, is a large condenser, c, of cast iron, 18 inches in diameter, and filled with water to p, a little above the level of the pipes. It is also furnished with a water valve, q, by which any danger of explosion, caused by the mounting of the liquid into the retorts, is entirely prevented, and the temperature is further reduced by placing the pipe in a large wooden trough, i, through which a current of cold water is constantly made to flow. The cylinder, c, is likewise made slightly to incline towards D, so that the condensed quicksilver may readily flow along its bottom, and passing through the vertical pipe, be collected in the closed iron chest, E, which is secured by a lock at h. The tube, D, is, from the commencement, closed at bottom, by dipping into a shallow iron cup, filled with mercury, and the progressive accumulation of the quicksilver is indicated by the position of the graduated iron float, k. These retorts, like those employed in

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the manufacture of gas, are constantly maintained in a uniform state of ignition, and thus the damage done to the joints is entirely obviated. Each retort will contain a charge of ore weighing 5 cwts., from which the metal is almost totally expelled in the course of three hours.

This apparatus is superior in principle to those already described, and is said to be particularly adapted for the treatment of the richer varieties of ore.

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# (464)

### LEAD.

### Equiv. = 103.56. Density = 11.35.

LEAD is a soft metal of a bluish-grey colour, and, when recently cut, possesses a strong metallic lustre; on exposure to the air it becomes rapidly tarnished, and acquires a superficial coating of the carbonate of the protoxide.

Lead is both malleable and ductile, possessing the former property to a considerable degree; but its tenacity is inferior to that of nearly all the other ductile metals. It is flexible and inelastic, and fuses at about 612° Fahr. When slowly cooled, imperfect octahedral crystals are readily obtained. At a red heat, lead becomes sensibly volatile, but not to a sufficient extent to admit of its distillation.

When kept in a state of fusion, in contact with the air, rapid oxidation takes place. At first the surface of the metallic bath becomes covered by an iridescent pellicle, which is quickly converted into a powder of a reddish-yellow colour. At a red heat this oxidation of the metal proceeds with great rapidity; and it becomes necessary, in order to continue the operation, that the oxide which gradually melts should be drawn off for the purpose of exposing a fresh metallic surface.

Lead, exposed to the influence of a damp atmosphere, quickly absorbs oxygen, and when acid vapours are likewise present, this action is much accelerated. This oxidation of the metal is induced even by the presence of the weakest acids, and particularly by carbonic acid, which gives rise to the formation of an oxide which, by subsequently combining with the acid present, affords a white carbonate of lead. Even distilled water, from its affinity for oxide of lead, determines the oxidation of that metal; and from this cause leaden cisterns are rapidly corroded when used as reservoirs for pure water. A bar of lead, placed in distilled water and exposed to the air, rapidly becomes coated with a white coating of hydrated oxide, which subsequently absorbs carbonic acid, and is thus converted into a hydrated carbonate of lead, which frequently forms distinct nacreous scales on the surface of the metal. In these cases the water is invariably found to hold a portion of lead

in solution, which is readily proved by its becoming brown on passing through it a current of sulphuretted hydrogen gas.

From the tendency exhibited by lead to form soluble salts, it ought never to be used for the manufacture of tanks in which water for domestic purposes is to be kept, as, from the poisonous nature of these compounds, the worst effects have frequently resulted.

The action of water on lead is, however, found to be much diminished by the presence of small quantities of various salts, and particularly sulphate of lime, which has the property of almost entirely preventing the oxidation and solution of this metal.

The lead of commerce often approaches chemical purity, and is then extremely soft and malleable. When lead of still greater purity is required, it may be procured by reducing in a lined crucible oxide of lead obtained by the decomposition of crystallised nitrate of lead. Lead is but feebly attacked by hydrochloric acid, even when concentrated and boiling. Weak sulphuric acid does not act on lead when the air is excluded; but if heated in strong sulphuric acid, sulphurous acid is evolved and sulphate of lead formed. The only proper solvent for lead is nitric acid, which oxidises it rapidly, and forms with its oxide a salt readily crystallising on cooling in opaque octahedrons.

#### ORES OF LEAD.

Lead is rarely found in a native state, but is usually in combination with one of the non-metallic elements, particularly sulphur. It also occurs with oxygen, selenium, arsenic, tellurium, and various acids. The ores of lead, with the exception of plumbo-resinite, are fusible before the blowpipe, and when fluxed with a little carbonate of soda on a charcoal support, yield a globule of metallic lead. The metal thus obtained passes off in fumes when heated in the outer flame, and stains the charcoal of a yellow colour.

Native Lead.—The characters of native lead are precisely similar to those of ordinary commercial lead. It is a rare substance, of which specimens have been found associated with galena in the county of Kerry, Ireland; and in an argillaceous rock near Carthagena, in Spain. Native lead has also been procured at Alston Moor, in Cumberland, where it occurs, disseminated with galena, in a siliceous rock.

Oxide of Lead; Massicot; Bleiglatte.—Is a pulverulent mineral of a bright red colour, sometimes mixed with yellow, and is a mixture of different oxides of lead, affording a metallic globule when heated on a charcoal support before the blowpipe. It usually occurs associated with galena, and is found in small quantities in many lead mines, particularly in those near Aix-la-Chapelle, and at Grass Chapel, in Yorkshire. From the comparatively small quantities of this ore which occur, it is of but little practical importance to the metallurgist.

**Chloride of Lend;** Plomb chloruré; Salzsaures Blei von Mendip. —Chloride of lead occurs in the Mendip Hills, in the form of lamellar shining masses, of a greyish-white colour. It is usually found deposited on a matrix of black oxide of manganese, and has a specific gravity of 7.07. When treated before the blowpipe, it decrepitates, and fuses into a globule of a yellowish-white colour: if heated on a charcoal support, metallic lead is obtained. Its primitive form appears to be a right rhombic prism under an angle of 102° 27'. This, although an exceedingly rare mineral, is likewise found in the lavas of Vesuvius.

Sulphide of Lead; Galena; Galène; Bleiglanz.-This mineral crystallises in the cubic system, and occurs both in the primitive and variously modified forms. Its cleavage, which is readily obtained, is cubic, and extremely perfect. It more rarely occurs in a finely granular state, and is sometimes found in fibrous masses. Compact specimens, although occasionally met with, are of comparatively rare occurrence. Its colour and streak are lead-grey; fragile; lustre metallic; specific gravity from 7.5 to 7.7. When pure it is composed of lead 86.55, and sulphur 13.45. Its composition is represented by the formula PbS. The lead in this mineral is almost invariably, to a greater or less extent, associated with silver, which appears to replace it according to the laws of isomorphism. When silver is thus present in the ore, it receives the name of argentiferous galena, and becomes a valuable source of that metal.

The analysis of an argentiferous galena from Schemnitz afforded to Beudant the following results :---

Lead, .					
Silver, .					
Sulphur,					13.40
				-	
				1	00.00

It also frequently happens that galena, in addition to the sulphide of silver, likewise contains variable quantities of the sulphides of antimony and bismuth. The first of these substances often appears to alter in a certain degree the characters of the mineral; and those specimens of which the laminæ are curved, as well as those which present a bright steely fracture, will generally, on examination, be found to contain this metal.

The veins producing galena occur in granite, limestone, argillaceous, and sandstone rocks, and frequently yield at the same time ores of copper, silver, and zinc. The matrix on which this ore has been deposited is, in most cases, either quartz, carbonate of lime, fluor spar, or sulphate of baryta. The rich lead mines of the West of England occur in clay-slate; those of Derbyshire, and the other northern districts, are situated in limestone, which also contains the extensive deposit of Bleyberg, and the neighbouring districts of Carinthia. In the Upper Hartz, and at Prizibram in Bohemia, the lead mines are found in clay-slate; at Freyberg in Saxony, in gneiss; at Sahla in Sweden, in crystallised limestone; and at Lead Hills in this country, in grauwacke. Valuable deposits of galena are also worked in various parts of France, and particularly at Huelgoat and Poullaouen, in Brittany; at Pontgibaud, Puy-de-Dôme, and at Villefort in the department of Lozère. In Spain, sulphide of lead is extracted in Catalonia, Grenada, the granite hills of Linares, and elsewhere. In the Netherlands, galena occurs at Vedrin, not far from Namur; in Savoy; Bohemia; at Joachimstahl, where the ore is principally worked for silver; and in Siberia, where argentiferous galena occurs in limestone in the Daouria mountains. Extensive deposits of this ore likewise occur in the United States of America, particularly in those of Missouri, Illinois, Iowa, and Wisconsin.

Cuproplumbite is a variety of galena containing 24.5 per cent. of sulphide of copper. It is a rare mineral, obtained from Chili.

*Dufrenoysite* is an arsenical ore of a dark steel-grey colour, from the dolomite of St. Gothard.

Selenide of lead; Clausthalite is a mineral of a lead-grey colour and granular fracture. When heated before the blowpipe it gives off the odour of horse-radish. It occurs in quantities too small to render it of any practical value as an ore of lead.

**Carbonate of Lend;** Plomb carbonaté; Blei Carbonat.—This mineral is characterised by its white colour and adamantine lustre. It is found in acicular crystals, in radiated and compact masses, in concretions, and in earthy deposits. All these varieties, with the exception of the last-mentioned species, possess the peculiar lustre belonging to white lead. It sometimes happens that crystallised specimens of this substance are nearly black; this arises from the presence of small quantities of sulphide, probably due to the decomposition of galena, with which carbonate of lead is usually found associated. It is an extremely brittle mineral, and, when amorphous, exhibits a conchoidal fracture. When treated with nitric acid, it dissolves, with evolution of carbonic acid gas : before the blowpipe it decrepitates, but when heated on a charcoal support, affords a button of metallic lead. Its specific gravity varies from 6.46 to 6.48.

Two specimens of this mineral afforded on analysis the following per-centage numbers :---

Cry	stals from L by Klapro	Crystals from Teesdale, by J. A. Phillips.				
Protoxide of lead Carbonic acid .	$\hat{1}$ $\hat{16}$	•••	. 83.55 . 16.52			
	98		100.07			

These results indicate a carbonate of lead having the formula PbO,  $CO_2$ . The amorphous and friable varieties are generally more or less contaminated by siliceous and earthy impurities. This mineral is found in splendid crystals at Lead Hills, Wan-lockhead, and in some of the Cornish mines, as well as in many other localities. When abundant, it forms a most valuable ore of lead, and frequently yields above 75 per cent. of that metal. From its dissimilarity to the other ores of lead, it was for a long time considered by miners to be of no value; but large quantities, which had been formerly buried in rubbish, are at the present time being excavated and worked with great advantage in many of the Spanish mines, as also at different points of the valley of the Mississippi, in the United States of America.

The white lead of commerce so extensively used as a pigment, is a carbonate of lead containing variable quantities of the hydrated oxide of the same metal. For this purpose it is prepared artificially by exposing metallic lead cast into thin bars to the united action of acetic and carbonic acids, by which means the sub-acetate at first formed is rapidly changed into carbonate by the presence of a large excess of carbonic acid. The acetic acid employed is usually obtained by the destructive distillation of wood, whilst a constant supply of carbonic acid is procured by the decomposition of thick layers of spent bark from the tan-yard. The lead to be operated on is laid over pots containing dilute acetic acid, and after being loosely covered with boards, is buried in tan to the depth of about 10 inches; on this is again placed another series of pots containing acetic acid : these are covered by a second layer of tan, and so on until 8 or 10 layers have been placed in the *stack*, which, from the fermentation which is rapidly set up, soon begins to evolve large quantities of carbonic acid. This action or working of the stack continues during from 10 to 12 weeks, and when it has nearly ceased, the layers of tan, lead, and pots are successively removed, and the white lead formed beaten from the surface of the unattacked metal to which it adheres. This is now ground in a mill with a due admixture of water, and when it has assumed the form of an impalpable paste is run off into large reservoirs, where it deposits in accordance with its density. The wet lead, after being removed from these cisterns, is first dried in large stoves by a steam heat, and subsequently ground in oil for the market.

**Sulphate of Lead**; *Plomb sulfaté*; *Bleivitriol.*—This substance crystallises in right rhombic prisms, which have an imperfect lateral cleavage, and are often slender and implanted. Specimens of sulphate of lead in amorphous masses, and in lamellar and granular fragments, are also occasionally found. Its colour is white, sometimes inclining to grey or green. Lustre adamantine, vitreous, or resinous. May be either opaque or perfectly transparent. When pure, it consists of 73 per cent. of oxide of lead, and 17 of sulphuric acid. If heated with carbonate of soda before the blowpipe, it affords a globule of metallic lead. Its composition is represented by the formula PbO,SO<sub>5</sub>.

This mineral is usually associated with galena, by the oxidation of the elements of which it appears to be formed.

Fine specimens of this ore are found in the lead mines at Lead Hills and Wanlockhead, as well as at Huelgoat in France, and in the States of Missouri and Wisconsin in America: it does not, however, occur in sufficient quantities to be regarded as an important ore of lead. Its density is about 6.3.

Cupreous Anglesite is a hydrated blue double sulphate of lead and copper, sparingly found at Lead Hills and Roughton Gill.

**Phosphate of Lead**; *Plomb phosphaté*; *Buntbleierz*.—This mineral occurs in hexagonal prisms of a bright green or brown colour. These crystals, which have a lateral cleavage, are often nearly transparent, and have sometimes a fine orange-yellow colour, derived from the presence of chromate of lead. This mineral has a specific gravity varying from 6.5 to 7.1, and affords a white streak.

Besides being found in crystals, it sometimes occurs in globules and reniform masses, with a radiated structure. The composition of two specimens of this substance examined by Karsten proved to be as follows :---

	Fre	om Bohemia.	From Cornwa				
Phosphate of lead .		89.268 .		89.110			
Chloride of lead .		9.918 .		10.074			
Phosphate of lime .							
Fluoride of calcium		0.137		0.130			
		You and the		1. 2 7			

#### 100.094

99.996

This composition indicates the presence of three equivalents of phosphate of lead united to one equivalent of the chloride of the same metal. Phosphate of lead is found in many of the lead mines in this country, and particularly in those of Cornwall, Lead Hills, and Wanlockhead. The phosphate of lead from Huelgoat, in Brittany, contains large quantities of alumina.

Arseniate of Lead much resembles in appearance the phosphate of that metal, but when heated evolves the odour of garlic.

A double phosphate of lead and lime, containing small quantities of chlorine and arsenic, has been found in Sweden.

**Chromate of Lead** is a mineral of a bright-red colour, which crystallises in oblique rhombic prisms, and blackens before the blowpipe; when heated on a charcoal support, it forms a shining slag containing numerous globules of metallic lead. It has a specific gravity of about 6, and when treated by nitric acid affords a yellow solution.

A specimen of chromate of lead, analysed by Berzelius, gave the following results :---

Oxide of lead				•	68.50
Chromic acid		•	•.		31.50

It follows from the above numbers, that this mineral is a simple chromate expressed by the formula PbO,  $CrO_3$ . Chromate of lead is the chrome yellow of painters, but is for this purpose artificially prepared by adding a solution of chromate of potash to a soluble salt of lead. It occurs in small quantities only, and is chiefly obtained from Brazil and Beresof in Siberia.

**Plumbo-resente** is a rare ore of lead, obtained at Huelgoat in Brittany, and from the Missouri mines in the United States of America. A specimen of this substance from Huelgoat, analysed by Berzelius, was found to be constituted as follows :---

Oxide of lead 40.14. Alumina 37.00. Water 18.80. Insoluble gangue 2.60. This mineral has a yellowish or reddish-brown colour, and possesses a lustre much resembling that of gum arabic.

All the other minerals containing lead are more or less rare, and in no instance occur in sufficient abundance to allow of being metallurgically treated as ores of this metal.

### ESTIMATION OF LEAD, AND ITS SEPARATION FROM OTHER METALS.

This metal is usually estimated by chemists in the form of sulphate, although it is sometimes weighed as anhydrous protoxide.<sup>1</sup> Lead is also frequently precipitated from its solution in the state of carbonate by the addition of an alkaline carbonate. The precipitate which is thus obtained is afterwards heated to redness in a porcelain crucible and weighed as protoxide. To prevent any error which might occur in the result through the reduction of

<sup>1</sup> Sulphate of lead contains 68.28 per cent., and oxide of lead 92.82 per cent. of metallic lead.

any portion of the oxide thus obtained, a drop of nitric acid should be added to the oxide after its ignition; on again heating this, the nitrate of lead at first produced is entirely decomposed, and pure protoxide fit for weighing is the result. Precipitated carbonate of lead should not, however, be calcined in a platinum vessel, as, however carefully the matter may have been separated from the filter on which it has been collected, small filaments of the paper are liable to remain in contact with it, and these, by effecting the reduction of a portion of the oxide, would cause the destruction of the vessel in which the operation is conducted. In calcining the carbonate employed in the estimation of this metal it should first be carefully removed from the filter, which is to be burned apart, and its ashes added to the calcined carbonate; since, if this precaution were not attended to, a large proportion of the resulting oxide would be reduced by the carbon of the filter. When sulphate of lead is to be calcined, the operation may be conducted in a platinum crucible, provided that the portion which separates readily from the filter be alone introduced. The filter, with its adhering sulphate, should then be placed in a porcelain crucible, and ignited; to the residue thus obtained a drop of sulphuric acid is subsequently added, and after heating to redness, the residue may be considered as sulphate of lead, and its weight added to that of the portion detached from the filter at the commencement of the operation.

Lead is separated from the alkaline metals either by a current of sulphuretted hydrogen gas, or by the addition of a soluble sulphate or carbonate. It is separated from magnesia, alumina, iron, manganese, chromium, cobalt, nickel, zinc, and many other bodies, by the alkaline sulphates or sulphuretted hydrogen. Cadmium and copper are separated from lead by the addition of an alkaline sulphate to their solution in nitric acid. From titanium, lead is separated by passing a current of sulphuretted hydrogen through their strongly acid solution, by which means the lead is entirely precipitated as sulphide, whilst the titanium remains in solution. Lead is separated from tin by first precipitating together the two metals by a carbonated alkali, and then treating the calcined precipitate with nitric acid. By this means the oxide of lead is dissolved in the form of nitrate, whilst the tin remains in the state of insoluble stannic acid. This is separated by filtration, washed with distilled water, dried, and weighed.

#### ASSAY OF LEAD ORES.

The ores of lead may, for the purposes of assay, be divided into two classes.

The 1st class comprehends all the ores of lead which contain neither sulphur nor arsenic, or in which these bodies are present in small proportion only.

The 2d class comprises sulphide of lead or galena, together with all lead ores containing arsenic, or sulphur or arsenic, or sulphuric acid.

From the facility with which this metal is sublimed when strongly heated, it is necessary to conduct the assay of its ores at a moderate temperature, as a notable quantity of the reduced metal would otherwise be driven off in the state of vapour.

The furnace best adapted for making lead assays is constructed similarly to that used for the fusion of the ores of iron, but is of much smaller dimensions. For this purpose, the internal cavity for the reception of fuel should be 9 inches square, and the height of the throat from the fire-bars about 13 inches. For ordinary ores, a furnace 8 inches square and 12 inches in depth will be found amply sufficient; but as it is extremely easy to regulate by a damper the heat of the larger apparatus, it is sometimes found advantageous to be enabled to command a higher temperature.

A furnace of this kind should be connected with a chimney of at least 30 feet in height, and requires to be supplied with good hard coke, broken into pieces of about the size of an egg.

Treatment of Ores of the First Class.—The assay of ores belonging to this class is a very simple operation, care only being required that a sufficient amount of carbonaceous matter be added in order to effect the complete reduction of the metal, whilst such fluxes are supplied as will afford, by combining with the siliceous or earthy matter present, a liquid and readily fusible slag. The mineral to be assayed is first pounded in an iron mortar, and passed through a sieve of fine wire-gauze. Those portions which remain on the meshes are again crushed until the whole has been passed through, since if this were not attended to, a fair sample of the ore could not be obtained, as the more sterile portions being usually the hardest are the last to become sufficiently crushed.

When the particles of ore have been properly reduced in size, 400 grains may be weighed out and well mixed with 600 grains of dry carbonate of soda, and from 50 to 60 grains of powdered charcoal, according to the supposed richness of the mineral.

This is now introduced into an earthen crucible of such a size as to be not more than two-thirds filled by the mixture, and on the top of the whole is placed a thin layer, either of carbonate of soda or common salt. The crucible and its contents are then placed in the furnace and gently heated, care being taken so to moderate the temperature that the mixture of ore and flux, which soon begins to soften and enter into ebullition, may not swell up and flow over the sides. If the effervescence becomes too strong, it must be checked by partially removing the crucible from the fire, and also by a due regulation of the draught by means of the damper.

When the boiling has subsided, and no more gas is given off, the heat is again raised during a few minutes and the assay completed. During the process of reducing the metallic oxide or carbonate, the heat should not exceed dull redness : but in order to complete the operation, and render the slags sufficiently liquid to admit of the accumulation of the lead in one button at the bottom of the crucible, the temperature must be increased to bright redness.

When the contents of the pot have been reduced to a state of tranquil fusion, it must, by the aid of proper tongs, be removed from the fire, and, after having been tapped gently against some hard body to collect the lead in a single globule, be set aside to cool. When the operation has been successfully performed, the cooled slag will present a smooth concave surface, with a distinct vitreous lustre. As soon as the crucible has become sufficiently cold, it is broken, and the button of lead carefully extracted. To remove from it the particles of adhering slag, the metallic button is hammered on an anvil, and afterwards washed and rubbed with a hard brush. If any portions of the slag adhere so firmly as not to admit of being readily removed by mechanical means, it may, in most instances, be separated by placing the button for a short time in a little dilute sulphuric acid, by which the slag is dissolved, whilst the metallic button remains unaffected. When the ore has been properly fluxed, and consequently a liquid slag obtained, the whole of the metallic lead will have collected in one mass at the bottom of the pot: but when a sufficiently fluid scoria has not been produced, it should be broken down in an iron mortar, and the metallic lead separated by washing and decantation.

Instead of employing carbonate of soda and powdered charcoal, the lead ore may be fused with 1½ times its weight of black flux, and the mixture slightly covered by a thin layer of borax. Very good results are also obtained by mixing together—

400	grains	of ore;	
400	"	carbonate of soda;	and
200	"	crude tartar.	

These ingredients, after being perfectly incorporated, are placed in an earthen crucible, and covered with a thin layer of borax.

The three foregoing methods yield equally good results, and afford slags containing but a very small portion of lead.

The assay of extremely rich lead products belonging to this class may, if required, be conducted without the use of any kind of flux, as when heated to redness in a lined crucible, they are readily and completely reduced. It is, however, advisable in all cases to add about 10 per cent. of carbonate of soda, by which the adherence of any metallic globules to the charcoal lining is effectually prevented. This method, although requiring a longer time than those already described, does not, even when rich ores are operated on, afford more satisfactory results.

When the mineral operated on, in addition to lead, contains other metals,-such as copper, silver, tin, or antimony, the button obtained will retain a greater or less proportion of these substances in the form of an alloy. If zinc be present in the ore, traces only of that metal will be discovered in the resulting button of lead, provided that the assay has been sufficiently heated: this, however, carries off a small portion of the lead. The oxide of iron contained in the ore is also reduced to the metallic state during the assay, but, unless too strong a heat has been employed, it remains in suspension in the slag. For commercial purposes the resulting button of lead is seldom subjected to a chemical examination, as the purity of the metal is usually judged of in accordance with its colour and softness; but when a more accurate knowledge of its constituents is required, it must be made to undergo the usual routine of metallurgic analysis. The carbonates of lead, which are imported into this country from Spain, are among the most important minerals belonging to this class, and are often extremely rich in silver.

Treatment of Ores of the Second Class.—This class not only comprehends galena, which is the most common and abundant ore of lead, but also comprises the sulphides resulting from various metallurgical processes, as well as the sulphates, phosphates, and arseniates of that metal.

*Galena.*—The assay of this ore of lead is variously conducted by different metallurgists; but one of the following methods is at present most commonly employed for commercial purposes.

The ore to be examined, after having been properly crushed and sifted, is fused either—

Firstly, with carbonate of soda, black flux, or cream of tartar. Secondly, with metallic iron.

Thirdly, with carbonate of soda or black flux, and iron.

Fourthly, with a mixture of nitre and carbonate of soda.

First Method—Fusion with an Alkaline Flux.—This operation is conducted in an earthen crucible, which is to be left uncovered until its contents are reduced to a state of tranguil fusion.

The powdered ore, after being mixed with three times its weight of dry carbonate of soda, is slowly and gradually heated in an ordinary assay furnace until the mixture has become perfectly liquid, when the crucible is removed from the fire, and, after having been gently tapped to collect any globules of metal which may be in suspension in the slag, is set aside to become cool. When cold, the crucible is broken, and a button of metallic lead, which must be cleaned and weighed, will be found at the bottom.

Instead of carbonate of soda, carbonate of potash or black flux may be used; but when the last-named substance is employed, a little longer time is necessary for the complete fusion of the mixture. Every 100 parts of pure galena will by this method afford from 75 to 77 parts of metallic lead, indicating a loss of from 7 to 10 per cent. on the contents of the ore.

Some of the older metallurgists were in the habit of first expelling the sulphur by roasting, and afterwards reducing the resulting oxide with about its own weight of black flux.

This process, from the extreme fusibility of the sulphides and oxides of lead, requires very careful manipulation, and at the best the results obtained are far from satisfactory. Pure galena, by this method, can rarely be made to afford above 70 per cent. of metallic lead.

Second Method—Fusion with Metallic Iron.—This process depends on the circumstance, that when galena is fused in contact with metallic iron, that metal becomes converted into protosulphide, whilst the lead originally combined with the sulphur is at the same time liberated. The amount of iron rigorously required for the decomposition of pure sulphide of lead is 22.6 per cent.; but it is found advantageous in practice to add a small excess of this metal, and 30 parts of iron to every 100 parts of galena are therefore commonly employed.

The iron used should be either in the form of small nails or fine wire cut into short pieces. This mixture of ore and metallic iron is placed in an earthen pot, of which it should fill about twothirds the capacity, and is covered with a thin layer of either carbonate of soda or borax. The crucible and its contents are afterwards heated to full redness, by which a well-fused and perfectly liquid slag is produced. When the contents of the pot are observed to be in a state of tranquil fusion, it is removed from the furnace and allowed to cool. It is then broken, and at the bottom will be found a button, which at first sight appears to have throughout a uniform composition, but on being struck with a hammer readily separates into two distinct parts. The upper portion consists of a bronze-coloured sulphide of iron, which at once crumbles under the hammer and is readily removed ; whilst the lower part consists of a button of malleable lead, which must be carefully cleaned and weighed. This process affords, from pure galena, about 78 per cent. of metallic lead: the loss appears to arise principally from the volatility of the galena, which begins to be driven off at a lower temperature than that required for its decomposition by the iron.

In the mining districts of North Wales this method of assay is conducted in a manner somewhat different to that just described. Instead of adding finely-divided iron to the ore, the pounded mineral is itself heated, and without the addition of any kind of flux, in a ladle made of that metal. This ladle or dish is formed out of a thick piece of sheet iron and provided with a lip, by which the reduced metal is to be poured off, and a short shank for affording a better holdfast to the tongs by which it is to be removed from the fire. The ore to be operated on is first coarsely powdered and well mixed, so as to ensure a fair sample: eight ounces are now weighed out and placed in the dish, which is covered with a lid of thin sheet iron, and gently heated in the fire of a smith's forge until the ore ceases to decrepitate. The temperature is then raised to full redness, and at the expiration of about fifteen or twenty minutes the decomposition of the sulphide will be completed. At this point the dish is removed from the fire and the reduced lead poured out into a mould of cast iron, whilst the slags and sulphide of iron formed are kept back in the dish by a piece of wood held before the spout for that purpose. The dish, together with the slags and sulphide of iron, is afterwards again placed in the fire and heated to bright redness, by which the last portions of metallic lead adhering to the scoria are obtained. The contents of the dish are now thrown away, as not containing any further amount of lead, whilst the metal which has been run off is carefully weighed. This apparently rude method affords, in experienced hands, remarkably good results, and which are likewise considered to approach very nearly to the practical returns obtained during the metallurgic treatment on the large scale. By this process, pure galena yields from 79 to 83 per cent. of lead; but with the poorer varieties of ore, such as those obtained from some of the Cornish mines, it is extremely doubtful whether satisfactory results could be obtained, since, from the infusibility of the associated gangue, numerous metallic globules would certainly be retained in the scoriæ. The ladles used for this purpose are rudely made of thick sheet iron, which if about 1-4th of an inch in thickness, will last during three or four separate assays.

Third Method—Fusion with Carbonate of Soda or Black Flux and Metallic Iron.—When galena and carbonate of soda are fused together out of contact with the air, a large proportion of the lead is liberated in the metallic form, but the scoria still retains a certain amount of that metal in the state of a double sulphide of lead and the alkaline metal.

If finely-divided iron be now introduced, the sulphide of lead contained in the slag will be decomposed; metallic lead is liberated, and the slag contains a double alkaline sulphide, in which iron will have replaced the lead formerly present. The earthy and siliceous matter constituting the gangue are also dissolved in the slag, without, to any great extent, impairing its fluidity. The quantity of black flux or carbonate of soda employed varies with the richness or sterility of the ore operated on; but even for the poorest varieties two parts of the alkaline reagent will usually be found sufficient. The iron, which is merely used to separate that part of the lead which has been dissolved by the alkali in the state of sulphide, need not be present in sufficient amount to effect the reduction of the whole of the lead contained in the ore treated. Two parts of black flux or carbonate of soda, and from 10 to 15 per cent. of metallic iron, either in the state of filings or in the form of small nails, will be found a convenient quantity to effect this purpose.

When the fusion is made with black flux, and the iron is in the state of filings, it will be proper not to add too large an excess, especially if the assay be conducted at a very high temperature, as in that case the resulting button of lead will contain a portion of iron. If, however, carbonate of soda be employed, the addition of a small excess of iron is attended with advantage, as it ensures the complete desulphuration of the galena without affecting the purity of the lead obtained.

Iron filings, when employed for this purpose, are also liable to become mechanically intermixed with the lead obtained, and thereby, to a certain extent, falsify the results. This inconvenience is obviated by the use of small iron nails, which are corroded only on the outside, and, at the termination of the assay, are found fixed in the upper surface of the button, from which they can without much difficulty be separated. Pure galena, when thus treated, yields from 75 to 78 per cent. of metallic lead.

Mitchell, in his Manual of Assaying, recommends the following process, which is a slight modification of that long employed at the Ecole des Mines. Two earthen crucibles are prepared by smearing their insides with black lead, such as that used for domestic purposes, and in each of these are placed, with their heads downwards, three or four ten-penny nails. Mix the ore to be assayed with its own weight of carbonate of soda, and, after having placed it in the pots, press it tightly down about the nails. On the top of this place about half an ounce of common salt, and above it an amount of dried borax equivalent to the weight of the ore operated on. The whole is now introduced into the furnace and gradually heated to redness; at the expiration of ten minutes the temperature is increased to bright redness, at which it is kept for another ten minutes, when the flux will be fused and present a perfectly smooth surface. When this has taken place, the pot is removed from the fire, and the nails are separately withdrawn by the use of a small pair of crucible tongs, care being taken to well wash each in the fluid slag until perfectly free from any adhering lead. When the nails have all been withdrawn, the pot is

gently tapped, to collect the metal into one button, and then laid aside to cool; after which it is broken, and the button of lead removed and cleaned in the usual way. The result is then verified by a second assay made in the other pot.

When carefully conducted, this process is said to afford from 84 to 84<sup>‡</sup> per cent. of metallic lead from pure galena. It is, however, liable to the objection, that the lead produced frequently contains fragments of iron, arising from the circumstance that the nails are most energetically acted on at the point of contact between the flux and the galena, which, when the slag becomes fused, occupies the lower portion of the crucible; and by this means portions of iron become detached and frequently adhere firmly to the button, from which there is sometimes considerable difficulty in removing them. In my own experiments I have never obtained by this process above 82 per cent. of metal from the purest specimens of galena, but it notwithstanding affords results sufficiently accurate for many commercial purposes.

Instead of adding metallic iron to the mixture of ore and flux introduced into the crucible, I have myself found it better that the pot itself should be made of that metal.

For this purpose, a piece of half-inch plate-iron, of good quality, is turned up in the form of a crucible and carefully welded at the edges; the bottom is closed by a thick iron rivet, which is securely welded to the sides, and the whole is then finished up with a light hammer on a properly-formed mandril. The crucible, when finished, should have the form represented fig. 178. To make an assay



in a crucible of this description, it is first heated to dull redness, and, when sufficiently hot, the powdered ore, intimately mixed with its own weight of carbonate of soda, and half its weight of crude tartar, is introduced by means of a long copper spout of the form represented fig. 179. On the top of this is placed a thin layer of dried borax, and the crucible, which, for the introduction of the mixture, has

been removed from the fire, is immediately replaced. The heat is now gradually raised to dull redness, during which time the contents gradually become liquid and give off large quantities of gas.



179.

At the expiration of from eight to ten minutes the mixture will be observed to be in a state of tranquil fusion, and the pot is now partially removed from the fire and its contents briskly stirred with a small iron rod; any matters adhering to its sides are

also scraped down to the bottom of the pot, which, after being again placed in a hot part of the furnace, is closed with an earthen cover and heated during three or four minutes to bright redness. The crucible is then seized by a strong pair of bent tongs on that part of the edge which is opposite the projecting lip, a, and after being removed from the fire its contents are rapidly poured into a cast iron mould of the form represented fig. 180. Another form of this mould is represented fig. 181. The sides of the pot are now

carefully scraped down with a chisel-edged bar of iron, and the adhering particles of slag and metallic lead added to the portion first obtained, by sharply striking the edge of the pot firmly held in the jaws of the tongs against the top of the cast iron mould. When sufficiently cooled, the contents of the mould are readily removed, and the button of lead, after being separated from

the adhering slag, is carefully cleaned and weighed. By this process pure galena yields on an average 84 per cent. of metallic lead, free from iron and perfectly malleable. This method of assaying is that in almost universal use in all leadsmelting establishments, and





181.

has the advantage of yielding good results with the whole of the various ores belonging to the second class. A larger amount of lead is, however, obtained by assay than can be procured from the same ores in the large way, and on this account the smelter usually makes an allowance of from 3 to  $5\frac{1}{2}$  per cent., in accordance with the nature of the mineral to be treated.

Instead of using iron pots, or adding metallic iron to the ores under examination, they may be fused with a mixture of black flux and oxide of iron or zinc, in which case a portion of iron or zinc is reduced, and the results before described obtained. This method, however, does not often afford satisfactory results, and is not so convenient as the processes in which metallic iron is employed.

The protosulphides of iron and zinc, when heated with galena and an alkaline carbonate, are partially decomposed, with the liberation of a certain portion of these metals, in the metallic form, and consequently the assay of ores containing sulphide of lead may be conducted by the aid of these reagents. This process, like the last, is however too inconvenient to admit of practical application, and, besides, does not afford satisfactory results.

Fourth Method—Fusion with Carbonate of Soda and Nitre.— When galena is treated with nitrate of potash, the whole of its sulphur is converted into sulphuric acid before any portion of the lead begins to be oxidised, and it consequently follows that if a suitable amount of nitre were employed, the desulphuration of the mineral will be completely effected, and the whole of the lead obtained in the metallic state. To prevent any loss which might arise from the deflagration which takes place, the ore is mixed with twice its weight of carbonate of soda, and to this, in accordance with the richness of the ore, is added from 30 to 35 per cent. of nitrate of potash. When too large a quantity of nitre is employed, a portion of the metal will be oxidised, and remain in the slag, causing a corresponding deficiency in the weight of the metallic lead, and therefore, as the right amount can only be ascertained by numerous experiments, this process is but badly calculated for estimating the lead contained in the mineral.

When, on the contrary, an ore contains silver, and that metal only is to be estimated, regardless of the amount of lead present, this process may sometimes be employed with considerable advantage, although it is generally less to be recommended than fusion with tartar and carbonate of soda, in a wrought iron pot, as before described. The assay by this process is very easily conducted; the fusion takes place readily, and without any bubbling, and the slag, which is very liquid, contains no metallic globules. In conducting this operation, the amount of nitre should, if possible, be so arranged as to afford the greatest quantity of metallic lead, but it is of especial importance that enough to destroy the whole of the sulphide be employed, as should the slag retain any unoxidised sulphur compound, a notable loss of silver will be experienced. If, on the other hand, too large a proportion of nitre has been made use of, the accuracy of the silver estimations will not be impaired, as the lead alone becomes oxidised, and the whole of the silver is contained in the residual metallic button.

Assay of Galenas containing Antimony.—Many of the ores of lead likewise contain a certain proportion of sulphide of antimony, and from such minerals the assayer can either obtain pure lead, or a mixture of the two metals in the form of an alloy.

To extract pure lead the mineral may be fused in an open crucible, with twice its weight of carbonate of soda, when the lead will be liberated in the metallic form, whilst the antimony, by becoming oxidised, unites with the alkaline base, and remains wholly suspended in the slag. The presence of antimony in the slag will also prevent its retaining any portions of the lead, and from this cause a tolerably exact separation of the two metals is readily obtained.

When, in addition to lead and antimony, the ore contains silver, it should be assayed by being heated with a mixture of carbonate of soda and nitre, by which the whole of the antimony will be oxidised and retained in the slag, whilst the lead and silver are obtained in the state of an alloy. In this case it is only necessary to add a sufficient amount of nitre to effect the total decomposition of the sulphide, as when the whole of the antimony and a portion of the lead has been oxidised, no loss of silver (which combines with the remaining lead) is experienced, but when, on the contrary, the slags still contain undecomposed sulphide of antimony, a large proportion of the silver escapes reduction to the metallic state.

When it is required to reduce at the same time both the antimony and lead, the ore may either be fused with black flux, in an earthen crucible, or be melted in an iron pot, according to the process before described.

The sulphates of lead are readily reduced by simple fusion with carbonate of soda in an earthen crucible, but when phosphorus and arsenic are present in ores of this metal, their assay should always be conducted in an iron pot, with a proper admixture of carbonate of soda tartar, and fused borax.

For commercial purposes lead assays are estimated in relation to the quantity of metal, in cwts. &c. contained in one ton of the ore treated. These calculations are dispensed with by the use of the following table, in which the quantity of ore operated on is supposed to be 400 grains.

and the second s	400 grains of Ore give grs. of Metal.	Weight of	Metal in a Ton	of Ure.	400 grains of Ore give grs. of Metal.	Weight of	Metal in a Ton	of Ure.	400 grains of Ore give grs. of Metal.	Weight of	Metal in a Ton	of Ore.	400 grains of Ore give grs. of Metal.	Welght of	Metal in a Ton of Ore.
	grs.	cwts.	qs.	lbs.	grs.	cwts.	qs.	lbs.	grs.	cwts.	qs.	lbs.	grs.	cw's.	qs. 1b3.
	60	3	0	0	80	4	0	0	100	5	0	0	120	6	0 0
1	61	3	0	5	81	4	0	5	101	5	0	5	121	6	0 5
1	62	3	0	11	82	4	0	11	102	5	0	11	122	6	0 11
	63	3	0	16	83	4	0	16	103	5	0	16	123	6	0 16
	64	3	0	22	84	4	0	22	104	5	0	22	124	6	0 22
-	65	3	1	0	85	4	1	0	105	5	1	0	125	6	1 0
	66	3	1	5	86	4	1	5	106	5	1	5	126	6	1 5
-	67	3	1	11	87	4	1	11	107	5	1	11	127	6	1 11
1	68	3	1	16	88	4	1	16	108	5	1	16	128	6	1 16
H	69	3	1	22	89	4	1	22	109	5	1	22	129	6	1 22
	70	3	2	0	90	4	2	0	110	5	2	0	130	6	2 0
	71	3	2	5	91	4	2	5	111	5	2	5	131	6	2 5
	72	3	2	11	92	4	2	11	112	5	2	11	132	6	2 11
	73	3	2	16	93	4	2	16	113	5	2	16	133	6	2 16
	74	3	2	22	94	4	2	22	114	5	2	22	134	6	2 22
	75	3	3	0	95	4	3	0	115	5	3	0	135	6	3 0
	76	3	3	5	96	4	3	5	116	5	3	5	136	6	3 5
	77	3	3	11	97	4	3	11	117	5	3	11	137	6	3 11
	78	3	3	16	98	4	3	16	118	5	3	16	138	6	3 16
	79	3	3	22	99	4	3	22	119	5	3	22	139	6	3 22

ASSAY TABLE FOR LEAD ORES.

II

						-									
400 grs. of Ore give grs. of Metal.	Weight of	Metal in a Ton	of Ure.	400 grs. of Ore give grs. of Metal.	Weight of	Metal in a Ton	of Ore.	400 grs. of Ore give grs. of Metal.	Weight of	Metal in a Ton	of Ore.	400 grs. of Ore give grs. of Metal.	Weight of	Metal in a Ton	of Ore.
grs. 140	cwts.	,	lbs. 0	grs. 186	cwts. 9		lbs. 5	grs. 232	cwts	. qs.	lbs 11	grs. 278	cwts.	qs.	lbs.
141	7	0	5	187	9	1	11	233	11	$\frac{1}{2}$	16	279	13	3 3	22
142	7	0	11	188	9	1	16	234	11	$\frac{2}{3}$	22	280	14	0	0
$\begin{array}{c}143\\144\end{array}$	$\frac{7}{7}$	0	$\frac{16}{22}$	189 190	9 9	$\frac{1}{2}$	$22 \\ 0$	$235 \\ 236$	11 11	3	$\begin{array}{c} 0 \\ 5 \end{array}$	$   \begin{array}{c}     281 \\     282   \end{array} $	14 14	0	$5 \\ 11$
144	7	1	$\begin{bmatrix} 22\\0 \end{bmatrix}$	191	9	2	5	237	11	3	11	283	14	0	16
146	7	1	5	192	9	2	11	238	11	3	16	284	14	Ő	22
147	7	1	11	193	9	<b>2</b>	16	239	11	3	22	285	14	1	0
148	7	1	16	194	9	2	22	240	12	0	0	286	14	1	5
$     149 \\     150   $	77	$\frac{1}{2}$	22	195 196	9 9	3 3	0 5	$\begin{array}{c} 241 \\ 242 \end{array}$	$\begin{array}{c} 12 \\ 12 \end{array}$	0	$\frac{5}{11}$	287 288	14	1	$\frac{11}{16}$
151	7	2	$\begin{array}{c} 0\\ 5\end{array}$	197	9	3	11	242	$12 \\ 12$	0	$11 \\ 16$	289	14 14	1 1	22
$   \begin{array}{c}     151 \\     152   \end{array} $	7	$\tilde{2}$	11	198	9	3	16	244	12	ŏ	22	290	14	$\frac{1}{2}$	0
153	7	<b>2</b>	16	199	9	3	22	245	12	1	0	291	14	<b>2</b>	<b>5</b>
154	7	<b>2</b>	22	200	10	0	0	246	12	1	5	292	14	<b>2</b>	11
155	7	3	0	201	10	0	5	247	12	1	11	293	14	2	16
156	777	3 3	5 11	$\begin{array}{c c} 202 \\ 203 \end{array}$	10 10	0	$\frac{11}{16}$	$\begin{array}{c c} 248 \\ 249 \end{array}$	12	1	$\frac{16}{22}$	294 295	14 14	$\frac{2}{3}$	$\frac{22}{0}$
$   \begin{array}{c}     157 \\     158   \end{array} $		э 3	$11 \\ 16$	203	10	0	22	245	$\begin{array}{c} 12 \\ 12 \end{array}$	2	22	296	14	9 3	5
159	7	3	22	205	10	1	0	251	12	$\overline{2}$	5	297	14	3	11
160	8	0	0	206	10	1	5	252	12	<b>2</b>	11	298	14	3	16
161	8	0	5	207	10	1	11	253	12	2	16	299	14	3	22
162	8	0	11	208	10	1	16	254	12	2	22	300	15	0	0
163	8	0	16	209 210	10	1	22	$255 \\ 256$	$\begin{array}{c c} 12\\ 12 \end{array}$	$\frac{3}{3}$	0	301	15	0	5
$   \begin{array}{c}     164 \\     165   \end{array} $	8	$\begin{array}{c} 0 \\ 1 \end{array}$	$\frac{22}{0}$	210	10 10	$\frac{2}{2}$	$\begin{array}{c} 0 \\ 5 \end{array}$	256	$12 \\ 12$	э 3	$\frac{5}{11}$	302 303	15 15	0	$\frac{11}{16}$
166	8	1	5	211	10	$\frac{2}{2}$	11	258	$12 \\ 12$	3	16	304	15	0	22
167	8	1	11	213	10	2	16	259	12	3	22	305	15	1	0
168	8	1	16	214	10	<b>2</b>	<b>22</b>	260	13	0	0	306	15	1	5
169	8	1	22	215	10	3	0	261	13	0	5	307	15	1	11
170	8	2	0	216	10	3	5	262	13	0	11	308	15	1	16
171 172	8 8	$\frac{2}{2}$	5 11	$\begin{array}{c c} 217\\218\end{array}$	10 10	3 3	$\frac{11}{16}$	$\begin{array}{c} 263 \\ 264 \end{array}$	$   \begin{array}{c}     13 \\     13   \end{array} $	0	$\frac{16}{22}$	309 310	15 15	$\frac{1}{2}$	$22 \\ 0$
173	8	$\frac{2}{2}$	16	219	10	3	$\frac{10}{22}$	265	13	1	0	311	15	$\frac{4}{2}$	5
174	8	$\overline{2}$	22	220	11	0	0	266	13	1	5	312	15	2	11
175	8	3	0	221	11	0	5	267	13	1	11	313	15	<b>2</b>	16
176	8	3	5	222	11	0	11	268	13	1	16	314	15	<b>2</b>	22
177	8	3	11	223	11	0	16	269	13	1	22	315	15	3	0
$\begin{array}{c} 178\\179\end{array}$	8	33	16 22	$\begin{array}{c} 224 \\ 225 \end{array}$	11	0	22	270	13 13	$\frac{2}{2}$	0	316 317	15	3	5
179	8 9	0	22 0	225	11 11	1	$\begin{array}{c} 0 \\ 5 \end{array}$	$\begin{array}{ c c } 271 \\ 272 \end{array}$	13	$\frac{4}{2}$	$\frac{5}{11}$	317	15 15	3 3	$\frac{11}{16}$
181	9	0	5	227	11	1	11	273	13	2	16	319	15	3	$\frac{10}{22}$
182	9	Ő	11	228	11	1	16	274	13	<b>2</b>	22	320	16	0	0
183	9	0	16	229	11	1	<b>22</b>	275	13	3	0	321	16	0	5
184	9	0	22	230	11	$\frac{2}{2}$	0	276	13	3	5	322	16	0	11
185	9	1	0	231	11	2	5	277	13	3	11	323	16	0	16
								1	1			l	4		

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Analysis of Galena.—The estimation of the lead contained in galena by the humid method, is for commercial purposes seldom resorted to, as sufficiently correct results may be obtained in a much shorter time by some of the processes just described. When, however, the analysis of this mineral becomes necessary, it may be conducted as follows :—

The ore, in a state of extreme division, is attacked at a gentle heat with dilute nitric acid, when sulphur will separate, and a solution of nitrate of lead be formed. The acid used for this purpose must be mixed with at least its own volume of distilled water; from the oxidation of the sulphur present in the ore, an insoluble sulphate of lead is formed, which remains with the insoluble gangue, and increases its weight.

For this reason it is in all cases advisable, after pouring off the solution of nitrate of lead obtained, and carefully washing the insoluble matters, to digest the residue for several hours with a strong solution of carbonate of soda, by which the insoluble sulphate of lead is converted into carbonate, and soluble sulphate of soda formed. The insoluble residue, after being separated from the sulphate and carbonate of soda by filtration, and well washed, is afterwards again treated with dilute nitric acid, by which the carbonate of lead is readily dissolved. This solution is subsequently added to that directly obtained by the action of weak nitric acid on the ore itself, and treated with a solution of sulphate of soda, until no further precipitation takes place. The sulphate of lead thus obtained is collected on a filter, washed, dried, and weighed, and from its weight, after calcination, is estimated the amount of lead originally present in the ore. The associated metals are afterwards separated from the filtrate from sulphate of lead, by the usual routine of mineral analysis. The amount of silver contained in galena cannot be correctly estimated by humid analysis, and must be ascertained by a process called cupellation.

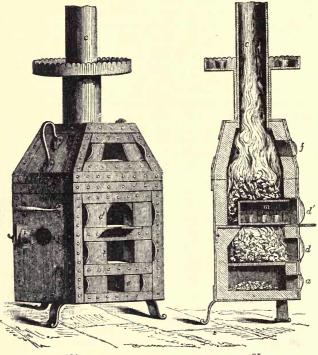
Estimation of the Silver contained in Lead Ores.—Cupellation.— From the large quantities of silver contained in many varieties of galena, and otherores of lead, it becomes necessary, in order to judge of their relative commercial values, to be enabled to ascertain with the greatest exactness the precise amount of this valuable metal furnished by the different specimens under examination.

To ascertain this, the button of lead obtained by the processes already described is subjected to cupellation in a furnace properly arranged for that purpose. This process is founded on the circumstance that silver, when exposed in a state of fusion to the action of the air, neither gives off perceptible vapours, nor is sensibly oxidised, particularly when a more oxidisable metal than itself is at the same time present. In order, then, to extract the silver contained in the metallic buttons obtained by the assay of lead ores, it is only necessary to expose them on some absorbent medium to such a temperature as may oxidise the lead, whilst the silver itself is not thus affected. The litharge produced is absorbed by the porous substance on



which the assay is supported, and nothing but a small button of pure silver ultimately remains in the metallic state.

182. 183. These supports, which are called cupels, figs. 182 and 183, are made of bone-ash, slightly moistened with a little water, and tightly consolidated by pressure in an iron mould.



184.

A convenient kind of furnace for the purpose of cupellation is represented figs. 184 and 185, of which the first represents an elevation, and the second a vertical section. The material of which these furnaces are made is wrought iron, which is lined

<sup>185.</sup> 

# ESTIMATION OF SILVER CONTAINED IN LEAD ORES. 485

with fire-clay, as shown in the drawing. The most important part of this apparatus is the *muffle*, *m*, which is a small D-shaped retort of fire-clay, closed at one of its extremities only, and furnished with perpendicular openings in the sides and end, in order to allow of a free circulation of air through its internal cavity. Fig. 186 represents a muffle, before its introduction into the

furnace. When fixed, it is so arranged that whilst one of its extremities is supported by a proper shelf, the other corresponds with the opening d', to the sides of which it is carefully luted by a little moistened fire-clay. This position of the muffle in the furnace allows



of its being heated on every side by a supply of ignited fuel, whilst the openings at its end and sides admit of the establishment of a current of air from the door, d', through the interior of the muffle to the cavity of the furnace. The interior of the muffle is, in this way, constantly traversed by a highly oxidising current of air, and the draught of the furnace is increased by the addition of a long chimney of sheet iron, c. To light this apparatus, a little ignited charcoal is introduced by the opening, d, and the cavity of the furnace afterwards filled with the same fuel, and the whole of the openings, excepting the ash-pit, a, closed by their proper slides. When the charcoal or coke is properly ignited, and the muffle has become red hot, six or eight cupels, which have been drying on the ledge around the chimney, are taken by the tongs, fig. 187, and placed on the floor of the muffle, which, to prevent its becoming corroded if any portion of lead be spilt on it, is previously covered by a thin layer of pounded bone-ash.

187.

The opening,  $d_i$  is now closed by its door, so as to prevent the introduction of a current of cold air, and the cupels are then raised to the temperature of the muffle itself. When this is the case, the door is again removed, and into each of the cupels is introduced, by a pair of slender steel tongs, a button of the lead to be assayed. The door is now a second time closed, during a few minutes, to facilitate the fusion of the metal, and on its removal each of the cupels is found to contain a bright convex metallic globule, in which state the assays are said to be *uncovered*. The air thus admitted rapidly converts the lead into litharge,

which, as fast as it is produced, is absorbed by the bone-ash of the cupel, and at the same time there arises a white vapour, which fills the muffle, and is gradually carried off through the openings in its sides. An annular stain is at the same time formed around the metal, which gradually extends, and penetrates into the substance of the cupel, in proportion as the metallic globule itself diminishes in size. When nearly the whole of the lead has been thus converted into litharge, and absorbed, the remaining bead of rich alloy appears to become agitated with a rapid circular movement, by which it seems to be made to revolve with great rapidity. At this stage of the operation, the agitation will be observed suddenly to cease, and the button, after having for a moment emitted a bright flash of light, becomes white and immoveable.

This phenomenon is called the *brightening* or *coruscation* of the metal, and a button of pure silver now remains on the cupel.

If the cupel were at this period abruptly removed from the muffle, the metallic globule would be liable to sprout or vegetate, by which a portion of its substance is not unfrequently thrown off and lost, whilst its surface is covered by numerous arborescent asperities. This effect appears to be chiefly produced by the sudden cooling of the surface exposed to the air, which, by its contraction, strongly compresses the liquid metal contained in the interior, and this, by bursting through the outside coating, escapes in the way described. To prevent this from taking place, and to guard against the loss of metal which would be liable to ensue, the cupel on which the button of silver has just brightened should be immediately covered by another, kept red hot for that The two are now withdrawn together, and allowed to purpose. remain on the ledge before the muffle, until the metal has become solidified, when the upper cupel may be removed, and the globule of silver is detached and weighed.

From the circumstance that silver becomes sensibly volatile at very elevated temperatures, it becomes necessary to make cupellations of this metal at the lowest heat by which the absorption of the litharge can be readily determined. If, however, the cupel be not sufficiently hot, an annular incrustation of crystallised litharge will begin to accumulate around its edges, and if at this point the fire be not immediately attended to, the deposit of oxide spreads over the whole surface of the metal, and its further oxidation is entirely stopped.

The temperature best suited for this operation is obtained when the muffle and the enclosed cupels are at a full blood-red heat, and the vapours which arise from the alloy curl gradually away, and are promptly removed by the draught. When the muffle is heated almost to whiteness, and the vapours rise to the crown of the arch, the temperature is too high, and when, on the contrary, the fumes lie over the bottom, and the sides of the openings in the muffle begin to blacken, a little more fuel must be added through the door, *f*, and the heat gradually raised. When the operation is conducted at the proper temperature, the cupel should be of a cherry-red colour, and the fused alloy very bright and convex. At the commencement of the operation the heat must be a little raised, for the purpose of fusing and uncovering the button, and just before the globule is about to brighten a slight elevation of temperature is again advantageous, but if a good cherry-red heat has been kept up during the working of the assay, this is by no means necessary.

The success of the experiment is likewise considerably influenced by the force of the draught passing through the muffle. When the current is too rapid, the cupel becomes cooled, and the lead is oxidised with greater rapidity than it should be: in this case the litharge produced is not absorbed by the test as fast as it is generated, and consequently the surface of the alloy is constantly covered by a layer of oxide of lead, by which it ultimately becomes protected from further oxidation. When, on the contrary, the current is too feeble, the assay remains a long time in the muffle, and a large amount of silver is lost by sublimation.

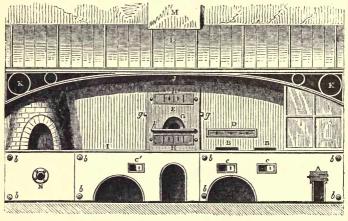
If an assay has been properly conducted, the residual button of silver is round, bright, and smooth on its upper surface, and beneath should be crystalline, and of a dead-white colour; it is easily detached from the cupel, and readily freed from adhering litharge. This globule is now removed by a pair of fine pliers, and flattened on a small steel anvil, by which the oxide of lead, which frequently attaches itself to it, becomes pulverised, and is easily removed by scratching with a small brush made of stiff hogs' bristles. The flattened disc is then examined by the aid of a powerful lens, in order to be sure that its surfaces are perfectly clean, and afterwards weighed in a balance capable of turning with 1-1000th of a grain.

The fuel employed in the furnace above described, consists, after it has once got into steady action, of small pieces of hard coke. When the ores of lead, in addition to silver, likewise contain gold, the residual button remaining on the cupel consists of an alloy of these metals, the separation and estimation of which will be treated of in a future chapter.

In metallurgic laboratories, where assays of gold and silver are being constantly made, the furnace above described is found inconvenient, on account of its small size. For this reason, stationary furnaces, forming part of the building of the laboratory, are commonly used.

A convenient arrangement of furnaces for the use of the metal-

lurgic chemist is represented fig. 188. This consists of a mass of brick-work bound together by strong plates of cast iron, and secured to the wall of the building by the bolts, b, which pass through it, and are fastened on the outside by screw nuts. A is the sand-bath door, B B are two furnaces; the first, 8 inches square, and 1 foot in depth, is well calculated for assays of lead ores, the other, 1 foot square, and 14 inches in depth, affords a sufficient heat for the fusion of assays of copper, tin, and even of iron ores. The draught is regulated by the dampers, D, which severally communicate with the furnaces, B B, and the sand-bath, A. The ash-pits, c, are provided with sliding doors, by which the currents of air entering the furnaces through the body of the brickwork are regulated. Beneath these are three arched recesses, for storing the broken coke. E is the cupelling furnace, pierced for a muffle at G, and provided with the double sliding doors, H H, by which the current of air passing through the arrangement is conveniently regulated.



188.

The opening for the muffle is considerably larger towards the front than where the muffle itself joins the brick-work, and before it, and at the same level, is placed the shelf, h, for the support of the cupels when withdrawn from the fire. The fuel is either introduced through the upper door, H, or from the top at J, which is covered by a heavy fire-tile, strongly bound with iron. gg are plugs stopping holes in the sides of the furnace, which, when open, are found convenient for tube operations. The openings, t, in the smaller furnace, fig. 184, are for the same purpose.

The total height of the cupel furnace, from the bars to the

throat-way of the draught, is two feet, and its internal dimensions one foot in width, and 14 inches in the direction of the length of the muffle. The muffle used in this furnace is 9 inches in length, and 5 inches in width. The small door, c', on the left of the cupelling furnace, belongs to a small brazier, used for holding lighted charcoal, when making organic analyses, for which purpose the apparatus may be placed on the iron slab at I. o is the hood of a small blast furnace, to be employed when extremely elevated temperatures are required, and which is supplied by a current of air from a powerful bellows at N.

The whole arrangement is covered by a glazed hood, L, supported by a trellis of wrought iron. Beneath this is a ventilator, communicating with the chimney, M, and which allows of being opened or closed at pleasure. This ventilator rapidly removes any deleterious fumes arising from the furnaces, without materially impairing the draught. The throat-ways of the different furnaces are placed at a distance of 5 inches from the top plates of the furnaces, which are protected from melting by the whole thickness of a fire-brick. With an arrangement of this kind, the heat necessary for the fusion, assay, and analysis of all kinds of minerals is readily obtained.

For commercial purposes, the silver contained in any given mineral is estimated in ozs. dwts. and grains, one ton of ore being taken in all cases as the standard of unity.

TABLE showing the weight of Silver to the ton of Ore, corresponding to the weight in grains obtained from 400 grains of Mineral.

If 400 grains of Ore give Fine Metal		ton o 11 yie	f Ore ld	If 400 grains of Ore give Fine Metal	One ton of Ore will yield				
grs.		dwts.		grs.		dwts.			
•001	0	1	15	•200	16	6	16		
.002	0	3	6	•300	24	10	0		
.003	0	4	21	•400	32	13	8		
•004	0	6	12	•500	40	16	16		
•005	0	8	4	•600	49	0	0 -		
•006	0	9	19	•700	57	3	8		
.007	0	11	10	•800	65	6	16		
•008	0	13	1	•900	73	10	0		
.009	0	14	16	1.000	81	13	8		
.010	0	16	8	2.000	163	6	16		
.020	1	12	16	3.000	245	0	0		
.030	2	9	0	4.000	326	13	8		
.040	3	5	8	5.000	408	6	16		
.050	4	1	16	6.000	490	0	0		
.060	4	18	0	7.000	571	13	8		
.070	5	14	8	8.000	653	6	16		
.080	6	10	16	9.000	735	0	0		
.090	7	7	0	10.000	816	13	8		
.100	8	3	8	10000	010	10	0		

#### LEAD.

Instead of operating on 400 grains of ore, many assayers prefer employing 1 oz. of mineral, and in this case the following table affords data for the necessary calculations.

Weight of Silver	to the Ton of	Lead Ore, o	corresponding to the	
weight in grain	s obtained from	n an assay or	n 1 oz. of Mineral.	

Grs.	Oz.	Dwt.	Grs.	Grs.	Oz.	Dwt.	Grs.
.001	"	1	11.840	•600	44	16	0.000
.002	44	2	23.680	•700	52	5	8.000
.003	44	4	11.520	•800	59	14	16.000
.004	44	5	23.360	•900	67	4	0.000
.005	66	7	11.200	1.000	74	13	8.000
.006	44	8	23.040	2.000	149	6	16.000
.007	66	10	10.880	3.000	224	0	0.000
.008	44	11	22.720	4.000	298	13	8.000
•009	66	13	10.560	5.000	373	6	16.000
.010	"	14	22.400	6.000	448	0	0.000
.020	1	9	20.800	7.000	522	13	8.000
-030	2	4	19.200	8.000	597	6	16.000
.040	2	19	17.600	9.000	672	0	0.000
.050	3	14	16.000	10.000	746	13	8.000
.060	4	9	14.400	20.000	1493	6	16.000
.070	5	4	12.800	30.000	2240	0	0.000
.080	5	19	11.200	40.000	2986	13	8.000
.090	6	14	9.600	50.000	3733	6	16.000
.100	7	9	8.000	60.000	4480	0	0.000
.200	14	18	16.000	70.000	5226	13	8.000
.300	22	8	0.000	80.000	5973	6	16.000
•400	29	17	8.000	90.000	6720	0	0.000
-500	37	6	16.000	100.000	7466	13	8.000

Manufacture of Cupels.-The bone-ash employed is first passed through a sieve of fine wire gauze, and afterwards mixed with water until sufficiently moistened to retain the mark of the fingers, when a handful is taken up and slightly squeezed. To cause the cupels when made to be sufficiently firm and resistant, a little carbonate of potash is added to the water employed for moistening the bone-ash. The amount of alkaline carbonate required for this purpose is exceedingly small, as a fragment of the size of a nut will be amply sufficient to add to a pint of water. Instead of water, some persons use sour beer, and in this case dispense with the use of any kind of alkali. The mould in which the cupels are formed, fig. 189, consists of a bevelled steel ring, b, and a die, a, made of the same metal and fitted with a wooden handle.  $T_0$ make the cupel, the cavity is nearly filled with the moistened boneash, which is first compressed slightly by the hand and afterwards with the die, which is tightly driven into the ring by the use of a heavy mallet, fig. 190. When sufficiently consolidated the die is

#### ENGLISH PROCESS OF LEAD-SMELTING.

withdrawn, and, by introducing a wooden cylinder which exactly

fills the aperture, the cupel is without difficulty removed. The use of the wooden cylinder is sometimes liable to crumble the edges of the cupel; and for this reason a loose iron plate, c, exactly fitting the bottom of the mould, is often introduced before the *a* bone-ash is placed in it. When this precaution is taken, the iron protects the bottom of the cupel, *b* and enables the operator to use considerable force without injury *c* to the edges of the newly made test. The iron plate has evi-



190.

dently to be replaced at each operation, and with the cupel before it, is again forced out of the mould. When made, the cupels are set aside to dry, and are then ready for use.

189.

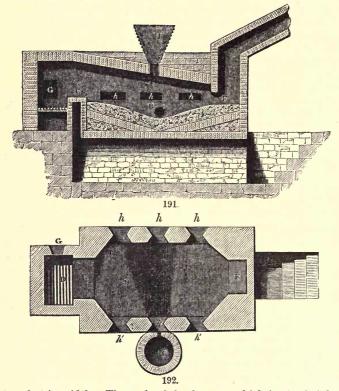
## METALLURGY OF LEAD .- ENGLISH PROCESS OF LEAD-SMELTING.

The metallurgic treatment of the ores of lead varies both in accordance with the composition of the minerals operated on, and with regard to the nature of the fuel to be obtained in the locality in which the mines are situated.

To describe all these different modifications would require more space than could be conveniently devoted to one metal, and I shall therefore merely endeavour to explain a few of the methods most commonly employed, and which may at the same time serve as types of the various metallurgic classes to which they severally belong.

The ores treated in this country principally consist of galena, which, before it comes into the hands of the smelter, has been deprived, by a careful mechanical preparation, of a large proportion of the earthy and siliceous ingredients with which it was originally associated.

The furnace in which the reduction of lead ores is usually effected in Great Britain is represented by figs. 191 and 192, of which the first represents a vertical section, and the second a ground plan. The sole is commonly about 10 feet in length and 8 feet in width, and is formed of fused slags obtained from preceding operations, and worked into the proper form when in a pasty and semi-fused state. Towards the centre of the hearth, at B, is a depression in which the fused metal accumulates; and at this point is situated the tap-hole, through which the reduced lead is, at a subsequent period, allowed to flow. The heat is applied by the fire-place, D, situated at one end, and, before reaching the furnace, has to pass over the fire-bridge, E, about one foot in height and



two feet in width. The arch of the furnace, which is at a height of about 14 inches above the top of the fire-bridge, gradually declines to within nine inches of the floor at the other extremity of the hearth : its greatest height from the cavity in the sole is about two and a half feet. At the end opposite to that in which is placed the fire-grate, is situated an opening in the masonry, F, which communicates with the flues in connection with a lofty chimney, by which the whole of the smoke and fumes escaping from the establishment are carried off. This channel for a short distance from the furnace is covered over with flat tiles closely jointed in fire-clay, as, from the tendency possessed by the lead fumes to fuse and choke the flues, it is necessary to be enabled to get readily at them for the purpose of their removal. The door, G, for supplying the coals to the grate, is situated on the face of the furnace called the labourer's side. In addition to this opening, there are three other holes, h, also placed in the same wall of the furnace. These measure about 9 inches by 12 inches, and are covered by iron plates, which can be removed without difficulty when the charge needs stirring, or a current of air is required.

The opposite face is known by the name of the working side, and, like the other, is furnished with three small doors, h', for cooling the furnace and working the charges. The floor, composed of furnace slag, is made up nearly to the small door on the labourer's side, but declines towards the other wall, so as to be 14 inches below the middle door; and here it communicates with the tap-hole, B, by which the lead is run out into a large cast iron pan, C, set in a niche a little under the furnace side. In the centre of the arch there is sometimes a small opening, fitted with a sheet iron hopper, I, in which a charge of ore is always kept ready for letting down as soon as that which is being worked in the furnace is withdrawn. This spout is provided with a damper, which is opened and shut by an iron lever, so that on its withdrawal the whole of the contents of the hopper at once fall on to the floor of the furnace.

As soon as the whole of the lead from the preceding charge has been drawn off, and the slags cleared out and removed, the hopper-shuttle is withdrawn, and another charge of ore allowed to fall on the floor of the furnace. The weight of lead constituting a charge for a furnace of this description differs both in accordance with its size and the quality of the mineral treated; in the North of England about 12 cwts. are commonly charged at one time, but in Wales from 20 to 24 cwts. are treated at one charge.

As soon as the charge has been let fall from the hopper, a labourer, placed at the back doors, spreads it out equally over the bottom of the furnace with an iron rake. The doors, together with the dampers communicating with the flues, are now closed, and the ore from time to time stirred about with an iron paddle, in order to expose fresh surfaces to the action of the air, which constantly enters into the laboratory through the spaces existing between the openings and sheet iron doors by which they are partially closed. During the first two hours which elapse after charging, but very little fuel is thrown on the grate, and the roasting is therefore principally carried on by the heat radiated from the sides of the furnace itself, and which had become heated to bright redness during the latter part of the preceding *shift*.

At the expiration of two hours from the commencement of the

operation, the foreman smelter opens the two front doors farthest removed from the fire, and throws into the furnace the rich slags skimmed off the surface of the lead obtained from the former charge after it has been collected in the external pot or lead-pan, c, and at the same time his assistant, through the back doors, turns over the roasted ore with a long iron paddle.

After a short time the tap-hole is opened for the purpose of running off the metallic lead obtained from the rich slag added, and the charge again worked over with an iron paddle as before described. At this stage the damper is slightly raised and a little fuel thrown on the fire; the interior of the furnace quickly assumes a dull-red heat, and the fusing matters, which begin to flow down into the interior basin, are brought back by the smelter to the part of the sole immediately before the fire-bridge, where they are uniformly spread over the surface by his assistant, who introduces his paddle through the back doors. A little quicklime is also thrown through the central opening on the bath of metallic lead which begins to accumulate on the depressed part of the sole. After a certain interval, the labourer again mixes with his paddle the various substances of which the charge is composed; whilst the smelter, with a large iron rake, pushes the slags from the surface of the inner basin back again to the raised part of the hearth directly before the fire-bridge. The doors are now left open for a short time, and the metallic lead which has been pushed down before the bridge with the slag flows back to the lower part of the sole.

The occasional cooling of the furnace is thought to facilitate the separation of the products, and thereby shorten the operation.

At the expiration of from three to three and a half hours, the damper is entirely opened, and the grate supplied with a larger amount of fuel; the doors are then all shut, and the furnace is left in that state during three quarters of an hour.

At a little more than four hours from the time of first charging, the doors are again opened, and the assistant stirs the contents of the furnace, for the purpose of facilitating the descent into the interior basin of the particles of metallic lead, whilst the smelter pushes back to him the slags which have accumulated in the lower part of the furnace. A little quicklime is also again added, for the double purpose of liberating a portion of oxide of lead, and rendering the slags less liquid and more easy of removal. More fire is now placed on the grate, and a little powdered coal thrown into the furnace; the doors are again shut, and remain closed during forty minutes. At the expiration of this period the doors are all metallic lead to flow into an exterior iron basin prepared for its reception. More quicklime is afterwards thrown into the inner reservoir, and the slags thus dried up are subsequently removed by the labourer through one of the back doors of the furnace.

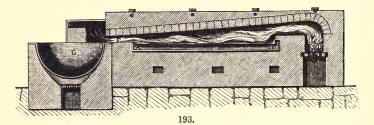
At Holywell, each ton of ore smelted consumes ten cwts. of coal; but at Grassington, in Yorkshire, where a more fusible galena is employed, and the operation is extended over a somewhat longer time, the same amount of ore is elaborated at an expense of  $7\frac{1}{2}$  cwts. only of fuel.

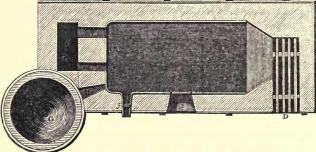
The whole shift of a smelting furnace, including the time necessary for casting the lead into pigs, occupies from  $5\frac{1}{2}$  to 7 hours.

In this process, the first effect produced on the ore by its gradual roasting is to convert a portion of the galena into sulphate of lead by the oxidation of its constituents; another part becomes changed into oxide, with the evolution of sulphurous acid gas; whilst a third quantity remains either entirely unaffected, or but slightly modified by the treatment to which it has been subjected. When, in the after periods of the operation, these three substances are strongly heated, a reaction takes place between the oxide and sulphate of lead formed and the undecomposed sulphide; this gives rise to the liberation of metallic lead, which is collected in the bottom of the furnace, and the formation of sulphurous acid, which escapes in the gaseous form, and is carried off by the flues to a high chimney, from which it escapes into the atmosphere. This repeated cooling of the furnace during the manipulation brings back the fused materials to a pasty condition, in which state they admit of being readily disintegrated by the action of the paddle, and consequently afford a larger surface exposed to the action of the atmosphere present in the apparatus. The porosity of the mass likewise facilitates the percolation of the streamlets of metallic lead, which thereby more readily gain access to the internal reservoir of the sole.

The drying up of the slags by the use of caustic lime tends to liberate the oxide of lead present in those compounds, and this, on being set free, reacts on any undecomposed sulphide which has resisted decomposition by roasting. It is also of service in mechanically thickening the scoriæ, and thereby rendering them fit for subsequent removal by the rake. The iron tools employed in this operation are rapidly attacked by the fused galena, and also tend to effect the liberation of the metallic lead. The small quantities of coal which are likewise added in the latter stages of the operation, aid in the reduction of the oxide formed, and prevent the oxidation of the reduced metal obtained by the other reactions.

**Calcining or Improving.**—The metal obtained by the process above described, almost invariably contains a sufficient amount of silver to render its extraction a matter of commercial importance; but, in addition to this, it is not unfrequently associated with antimony, tin, copper, and some other impurities, which require to be removed before the separation of the silver can be advantageously undertaken. When English ores have been operated on, the lead obtained is usually of sufficient purity to admit of being at once passed, in accordance with its richness, either to the refinery or desilverising pots; but when foreign, and particularly Spanish minerals have been treated, it is all but impossible to obtain good lead without the intermediate process of calcination. This operation consists of fusing the alloy in a reverberatory furnace of peculiar construction, and allowing it to remain, when in a melted state, exposed for a more or less considerable period to the oxidising influences present in the apparatus. By this treatment, the antimony, tin, and other metals, together with a portion of the lead, become oxidised, and are gradually removed from the surface of the bath by an iron rake; thus constantly exposing a fresh surface to the action of the gases of the furnace, until the greater portion of the impurity is removed, and a pure, or nearly pure, alloy of lead and silver is obtained.





The furnace in which this operation is conducted is represented figs. 193 and 194: fig. 193 is a vertical section, whilst fig. 194 shows the general arrangement of the ground plan. The sole of this arrangement consists of a large cast iron pan,  $\land$  B, 10 feet in length, 5 feet in width, 9 inches in depth at the extremity,  $\land$ , and 8 inches at the other. This is placed perfectly level, and rests on a mass of masonry 2 feet 6 inches above the floor, and is bedded on a thin layer of sand, in order that it may take in every part a good and equal bearing. Around this pan, but, to allow for expansion, not in contact with it, are built the sides on which the arch of the furnace is supported. This arch is, at the extremity,  $\land$  6 inches above the level of the sole pan, whilst at the other extremity, B, it is 1 foot 6 inches from the same line. The fire-place is 5 feet in length, and 1 foot 6 inches in width, and is divided from the lead-pan by a fire-bridge 2 feet 3 inches in width, and rising about 8 inches over the edge of the quadrangular iron basin.

At the other extremity of the furnace are the flues, E, by which the draught into the main chimney is established. The pan is likewise furnished with an iron lip, F, by which its contents can be run off into a tripod receiving-pot when sufficiently purified. The large iron pot, G, set in brick-work, is used for the purpose of fusing the pigs of impure lead to be operated on, which is afterwards laded into the calcining furnace by the aid of a sheet-iron spout introduced through the aperture, H, which, when not thus employed, is carefully shut by a small damper.

The charge of one of these furnaces varies from 6 to 8 tons; and before it can be laded in, the spout, F, which is grooved for the reception of a door, is closed by the introduction of a proper plate of sheet iron, behind which is placed a dam made of a firebrick firmly luted in its place with a little moistened bone-ash. The brick, together with the external iron plate, is notched at the lower extremity, so as to form a sort of tapping-hole at the level of the bottom of the iron pan.

When the dam has been properly arranged, and the fire has been lighted sufficiently long to heat the sole-plate to incipient redness, the fused metal is laded into the furnace, and the operation of calcination begins. The alloy which has been charged into the furnace soon becomes covered on the surface with a thick granular scum, which is frequently removed by an iron rake through the door, I, and a clean metallic surface thus constantly exposed. The length of time required for the purification of the lead necessarily depends on the nature and amount of the substance with which it is combined; and consequently some varieties of hard lead will be sufficiently improved at the expiration of twelve hours; whilst it is necessary in other instances to continue the operation during three or four consecutive weeks.

When the metal is in a fit state for tapping, a small portion

taken out with a ladle and poured into a small mould used for this purpose is observed, on cooling, to assume on the surface a peculiar flaky crystalline appearance, which, when once seen, is easily again recognised. Immediately that this appearance presents itself, the plug of bone-ash is withdrawn, and the lead run off, through a moveable iron spout, into a pot supported on a tripod stand, from which it is subsequently laded out into moulds.

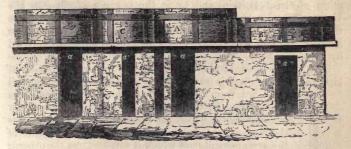
Concentration of the Silver contained in Lead—Pattinson's Process.—This method is founded on the circumstance, first noticed in the year 1829, by H. L. Pattinson, Esq., of Newcastle-on-Tyne, that when lead containing silver is melted in a suitable vessel, and afterwards suffered to cool very slowly with constant stirring, at a certain temperature, near the melting point of lead, small metallic crystals begin to form within the fluid alloy, which, as rapidly as they are produced, sink to the bottom, and, on being removed, are found to contain much less silver than the lead originally operated on : the still fluid alloy from which the crystals have been removed is at the same time rendered proportionally richer in silver.

The application of this discovery constitutes "Pattinson's Process," which, when the above detailed principles have been properly understood, becomes extremely simple. A series of eight or ten cast iron pots are set in a row, with a fire-place beneath each. These are each capable of holding about 5 tons of molten lead; and, on commencing the operation, that quantity of metal, which is called original lead, containing, it may be, about 10 oz. of silver per ton, is introduced into one of them placed about the middle of the series; this, when melted, is carefully skimmed with a small perforated ladle, and the fire immediately withdrawn from beneath the pot. The lead then begins very slowly to cool, and is constantly kept stirred with a long iron paddle or slice. In a short time small solid particles or crystals of lead begin to form among the fluid mass; and these, as they accumulate and fall to the bottom of the pot, are removed by means of a large perforated ladle, in which they are well shaken, and afterwards carried over to the next pot to the right in the series. This operation goes on until about four tons of crystals are taken out of the pot No. 4, in which we will suppose the original lead to have been melted, and have been placed in the pot No. 3, at which time the lead of the pot No. 4 will contain about thirty ounces of silver per ton, and that contained in No. 3 only about five ounces. The enriched lead in the bottom of pot No. 4 is then laded into the next pot, No. 5, to the left in the series, and the same operation repeated in pot No. 4 on a fresh quantity of lead.

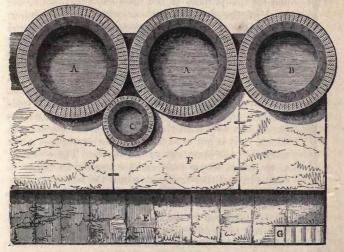
In this way original lead is constantly introduced, and the re-

## PATTINSON'S PROCESS.

sulting poor lead passes continually to the right, whilst the enriched alloy is passing towards the left; and as each pot in the series, when filled up with lead of its own quality as regards produce in silver, is continually crystallised, the poor lead passing to the right and the rich to the left, it evidently follows that the crystals from



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196.

the pots to the right must become gradually deprived of their silver, whilst the enriched lead, as it advances successively from pot to pot towards the left, becomes richer and richer; the final result being that at the end of the series the poor lead contains but a mere trace of silver, whilst the liquid alloy, on the other hand, becomes so rich, that a large plate of silver is obtained by submitting but a small quantity of it to cupellation. By these repeated crystallisations, the quality of the poor lead is likewise found to be much improved.

This process is now followed in nearly all the lead-mining districts of Great Britain, and by it the produce of silver in the United Kingdom has, within the last twenty years, been more than doubled. In addition to this, large quantities of lead are annually brought to England for the purpose of being desilverised by its application.

The arrangement of the pots in which the crystallisation of lead containing silver is carried on is represented figs. 195 and

> 196; but, from want of space, three only of the series are included in the woodcut. A A are the ordinary working-pots in which the crystals are obtained. B is the poor or market-pot, placed at the extreme right of the arrangement, and which is smaller than the others : from this pot the poor lead is laded out into the moulds, and for this purpose it is a little less raised above the level of the floor than those which are adjoining. During the working of the process, the ladle employed in taking out the crystals is liable to become chilled; and when this is the case, the lead adheres to it so firmly as to stop up the holes with which it is perforated. To remedy this inconvenience, as well as to prevent rich lead being carried over with the crystals, small vessels, full of fused lead, raised to a higher temperature than that of the larger pans, are placed between each two, with the exception of the market-pot, which, as it is not used for preparing crystals, is never worked in the same way as the others. These vessels, c, are called *temper-pots*, and are usually 18 inches in diameter, and therefore just admit the ladle and allow it to stand upright. The ash-pit, E, of the arrangement extends the whole length of the series, and is partially covered by the flooring, F, which is supported by a row of slender iron pillars. This is approached by a flight of steps, G, by which the workmen can descend for the purpose of attending to the fires, a.

> The ladle by which the crystals are removed from the pots, fig. 197, is about 16 inches in diameter and 5 inches in depth: the part which is of iron is about 4 feet 6 inches in length, and into the socket is inserted a wooden handle, which may be five feet in

197.

length. The bottom of the ladle is pierced with numerous holes for the escape of the liquid alloy; and, to prevent its breaking when full of crystallised metal, the part of the shank where it is welded to the bowl is made extremely thick and strong. When this strainer has been filled with crystallised lead, it is drawn out of the pot by the weight of the workman, who steps on the top of the brick-work and uses the wooden handle as a lever, by which he again lets himself down on the floor. On the edge of each pot is placed a large pig of lead, into the upper surface of which a bar of iron has been cast, and this serves as a fulcrum on which the shank of the ladle rests whilst it is being violently shaken by the workman, who, standing on a wooden bridge thrown over the ash-hole, applies all his force in jerking at the other extremity.

When the crystallised lead has been sufficiently drained by this treatment, the shank of the ladle is placed in a hook attached to a chain hanging from one of the beams of the roof, and is thereby swung over the pot next in the series to the right, where its contents are allowed to fall. The poor lead prepared by this process should never contain more than 10 dwts. of silver to the ton of metal; and the rich lead is seldom concentrated much beyond 500 ounces to the ton, as beyond this point the crystals obtained become too strongly charged with the more valuable metal.

**Parkes's Process for Desilverising Lead** — This invention is founded on the property possessed by zinc of uniting with the silver contained in argentiferous lead, and, when fused together, forming with it an alloy which is readily skimmed off from the surface of the metallic bath. Messrs. Neville & Co., who employ this process of desilverisation in their works at Llanelly, conduct the various operations as follows :—

The lead to be desilverised is first fused in a large cast-iron pot similar to those used for Pattinson's process, and by the side of this is placed a much smaller one, in which is melted the zinc to be employed during the operation. When the lead in the large pot has been completely fused, its surface is freed from dross by means of a small perforated iron ladle, and its temperature is then raised to the fusing point of zinc, or nearly so. The melted zinc is now added to the lead in the proportion of from 1½ to 2 lbs. for every ounce of silver contained per ton of the lead operated on, and the alloy is then well stirred and mixed together for about twenty minutes. When this has been done, the fire is withdrawn from beneath the larger pot, and, in proportion as it cools, a thick scum rises to the surface, and is skimmed off by means of ladles similar to those employed for the ordinary process of crystallisation. The alloy thus obtained consists of a mixture of lead and zinc, containing almost the whole of the silver originally present in the lead treated, and is subjected to a process of liquation in an inclined iron retort. By this means a large portion of the lead present is eliminated, whilst the zinc, together with the silver and traces of lead, remain in the retort. The lead thus separated from the alloy of zinc and silver contains on an average about 6 ounces of silver per ton. On treating this rich lead in an ordinary softening furnace, the zinc which it contains rises to the surface in combination with the silver, and is readily removed by skimming.

The argentiferous alloy remaining in the liquation retort is next removed to a Silesian zinc furnace, in which the zinc is separated by the ordinary process of distillation, and is condensed for further use, whilst the silver remains in the retort in combination with a little lead, and is more or less contaminated with the oxides of lead and zinc.

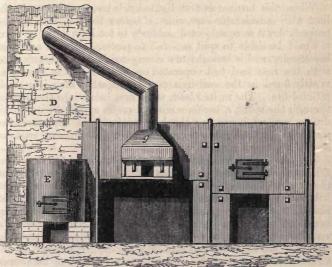
The silver thus obtained is, with the addition of a little lead, treated in an ordinary refining furnace; whilst the oxides of lead and zinc, which are also argentiferous, are added to the various silver ores smelted in the establishment. At Llanelly, each pot is capable of containing from 6 to 7 tons of lead, and yields from 17 to 18 cwts. of argentiferous skimmings. These skimmings, when treated in the first retort, yield about 80 per cent. of eliquated lead, and 20 per cent. of argentiferous matters, which are passed to the Silesian furnace.

The lead which remains in the larger pot after the removal of the argentiferous skimmings is at once removed to the calcining or improving furnace, from which the products obtained are softened lead and a very small quantity of argentiferous dross, which is added to that formed during the various other stages of the operation.

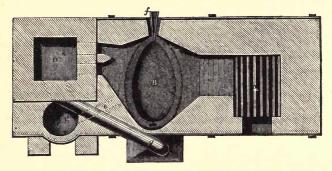
This method is said to be more economical than crystallisation, but it has the disadvantage of not separating the silver quite so effectually as Pattinson's process, and the lead produced is also harder and whiter than that obtained by the ordinary process. The lead treated according to Parkes's patent usually retains about one ounce of silver per ton.

**Refining of Silver.**—The extraction of the silver contained in rich lead is conducted in a cupel forming the bottom of a peculiarly arranged reverberatory furnace, called a refinery, figs. 198 and 199. In this operation, the litharge produced, instead of being absorbed by the substance of the cupel, is run off in the fluid state by a contrivance presently to be described. The fireplace, A, is about two feet square, and separated from the body of

the furnace by a fire-bridge 18 inches broad, so that the flame and heated air pass directly over the surface of the cupel, B, and from thence escape through the two openings, c, into the flue, D, in connection with the main chimney of the establishment. The cupel, or test, consists of an oval iron frame, surrounded by a ring four inches in depth; its greatest diameter being four feet, and its lesser about three. This frame is, in order the better to support the bottom of the cupel, provided with four or more crossbars, which are four inches in width and half an inch in thickness: the first of these is placed about nine inches from the fore part of the frame, and the other at equal distances from this bar to the other extremity of the rim. The test-frame is now beaten full of finely-powdered bone-ash, slightly moistened with water, containing a small quantity of carbonate of potash (pearlash), which has the property of agglutinating and giving consistency to the bone-ash when heated. The centre of the cupel, after the ring has been well filled with this mixture and solidly beaten down with iron rammers, is scooped out by a small trowel until the sides are left two inches in thickness at top, and three inches wide at bottom ; whilst the thickness of the sole itself is reduced to one inch above the surface of the iron cross-pieces. At the fore part of the test, called the breast, the width of the border is



increased to five inches; and a hole is here cut through the bottom which communicates with the passage or *gateway* by which the fluid litharge makes its escape.



## 199.

The test, when thus prepared, is placed in the refinery furnace, of which it forms the bottom, and is wedged at its proper height against an iron ring, or *compass-bar*, firmly built into the masonry. The height of the arch of the furnace above this bar is thirteen inches on the side of the fire-bridge, and eleven at the flues.

When this furnace is first lighted it is necessary to apply the heat with considerable care, since, if before the test had become properly dry it were subjected suddenly to too high a temperature, it would be liable to split and fall to pieces. As soon as it has become dry, and is brought to a cherry-red heat, it is nearly filled with the rich lead to be operated on, and which has been previously fused in the cast-iron pot, E, beneath which is a small pit-coal fire. The melted lead, when first laded into the furnace through the spout, e, becomes covered on its surface by a greyish dross; but, on increasing the heat to incipient whiteness, the surface of the bath uncovers, and a covering of ordinary oxide of lead or litharge begins to form.

The blowing apparatus, which furnishes the blast to the tuyere, f, is now set in motion, and forces the litharge from the back of the cupel up to the breast, and over the gateway, from which it falls through the aperture in the cupel into a moveable iron pot placed for that purpose on a level with the floor of the smelting house. The current of air which may be supplied either by a ventilator or bellows, not only sweeps off the litharge from the surface of the lead, but also furnishes the oxygen required for its formation, care being at the same time taken to keep up the proper degree of heat. In proportion as the surface of the lead becomes depressed by its continual oxidation and the constant removal of the litharge formed, more metal is added from the melting pot so as to raise it to its proper height, and in this manner the operation is continued until about five tons of rich lead have in successive portions been introduced into the test.

The contents of the cupel are now so far reduced in volume that the whole of the silver contained in the metal operated on may remain in combination with only two or three hundred weight of lead, which is now removed from the test by making a hole through the bone-ash forming the bottom. When the rich lead has been thus removed, the tapping-hole is again closed by a pellet of moistened bone-ash, and another charge is immediately introduced. After a sufficient number of these parcels of rich lead have been obtained as are found by assay to be capable of yielding a cake of silver weighing from three to five thousand ounces, they are again melted down, and placed in a cupel, where the process of extracting the pure silver is completed. The test used for this purpose differs from that in which the lead is first introduced, inasmuch as it is so hollowed out in the bottom as to give thickness to the resulting plate of silver, and allow space for the removal of the litharge around its edges after the operation has been completed. The brightening of the pure silver at the moment of separating the last traces of combined lead, takes place in the large furnace as in the small cupel, and the aborescent forms produced on the surface of the plate at the moment of cooling are frequently of the most beautiful description. The small hood and chimney, g, shown in the woodcut, are for the purpose of carrying off the fumes of lead generated during the operation, and which, if breathed by the workmen, would be productive of the most prejudicial effects.

Previous to the discovery of the present methods of improving and enriching the metal obtained directly from the ores, none but moderately rich leads could be treated for the silver which they contained, as they were on their reduction immediately sent to the refinery, where the combined silver was extracted, whilst the whole of the associated lead became converted into litharge, which had, at a considerable expense, again to be reduced to the metallic state. This method of treatment not only involved the expenditure of a large amount of coal, but likewise the loss of at least 7 per cent. of the lead operated on; and consequently lead that did not contain from 9 to 11 oz. of silver per ton, did not admit of being profitably refined. When the lead and silver were also associated with tin or antimony, the difficulty and expense of this process were much increased, and proportionally richer ores were consequently required in order to render its extraction a profitable undertaking. By the improved methods just described, lead containing but 3 oz. of silver to the ton of metal may be refined with advantage, as from the circumstance of the whole of the silver being concentrated in about 1-tenth of the weight of lead, a very small portion of that metal is dissipated during the cupellation. When very rich lead is operated on, the plate of silver is sometimes directly worked off, instead of tapping the rich alloy from the cupel in the way above described. The last portions of litharge obtained from the refining furnace carry off with them a notable quantity of silver, and are, therefore, together with the reduced cupel bottoms, again treated for the extraction of that metal.

Reducing.—The reduction to the metallic state of the litharge from the refinery, the pot dross, and the mixed metallic oxides from the calcining pans, is effected in a reverberatory apparatus somewhat resembling in form the smelting furnace, except that its dimensions are smaller, and that the sole, instead of being lower beneath the middle door than at any other part, gradually slopes down from the fire-bridge to the flue at the opposite extremity, where there is a depression, in which is situated the tap-hole; this constantly remains open, and from it the reduced metal continually flows out into a small iron pot placed on the side of the furnace, for its reception: from this it is subsequently laded into proper moulds, usually bearing the name of the smelting company by which it has been prepared.

Before being thrown into the furnace, the litharge is intimately mixed with a quantity of small coal, and is then charged on that part of the hearth which lies immediately before the fire-bridge. To prevent the fused oxide from attacking the bottom of the furnace, and also to afford a sort of hollow filter for the liquid metal, the workman, before charging the substance to be reduced, covers the sole with a layer of about two inches in thickness of bituminous The heat of the furnace very soon causes the ignition of coals. this stratum, and it therefore quickly becomes burnt to the state of a spongy red-hot cinder, upon which the mixed litharge and carbonaceous matter is charged. The reducing gases present in the furnace, aided by the small coals in the charge itself, cause the reduction of the litharge, which, assuming the metallic form, gradually flows through the interstices in the cinder, and falls into the depression at the extremity of the hearth, from whence it gradually flows through an iron spout into the external pot in which it is collected. The surface of the charge is, during its elaboration, frequently scratched over with an iron rake, pine, for the double purpose of exposing new surfaces to the action of the

furnace, and also to enable the reduced lead to more readily flow down to the other end of the sole, and which, if too long exposed to the action of the heated gases, would experience considerable loss from sublimation into the flues. Fresh quantities of the mixture of litharge and small coal are from time to time added, in proportion as that already thrown into the furnace disappears, and at the end of the shift, which usually lasts twelve hours, the cinder floor is broken up and *pined*, together with the residual matter in the furnace.

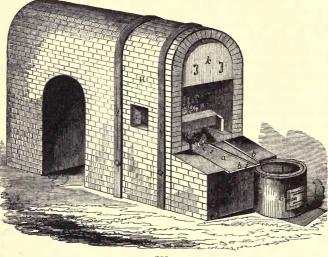
The temperature at this period is likewise a little raised, and the last quantities of lead extracted. A furnace of this kind, having a sole six feet in length and five in width, will, from ordinary litharge, afford about three tons ten hundred weight of lead in the course of twenty-four hours.

Before reducing the dross from the calcining pans, it is usually ground with a certain admixture of pit coal under a pair of heavy edge-runners, by which it becomes more equally intermixed with the carbonaceous matters, and the composition of the mass throughout is rendered more uniform.

The hard lead obtained by the reduction of the dross is again carried to the calcining furnace, where it is a second time subjected to a current of oxidising gases.

Scotch Furnace, or Ore Hearth.—In many parts of England, and particularly in the counties of Durham, Cumberland, and Northumberland, the smelting of lead ores is principally conducted in an arrangement called a Scotch furnace, or ore hearth. This consists of a rectangular cavity of masonry, twenty-four inches in length and about twelve in breadth; its depth varies from twentytwo to twenty-six inches, and the whole of its internal surface is lined with cast iron. The bottom, which consists of but one casting, is surrounded by a ledge two inches and a half in thickness and five inches in height; except on the side facing the work-stone, a, fig. 200, which is two feet ten inches in breadth, and about one foot six inches in the other direction.

This is also surrounded by a narrow ledge, b, on every side except at c, opposite the hearth bottom. This plate is placed with a fall of about six inches in its whole width; its upper side rests on the ledge surrounding the hearth-bottom, or in some instances is united to it, and only forms one casting: when this is not the case, the joint between the two is closed, and made lead-tight by a cement composed of a mixture of bone-ash, moistened with water, and well kneaded together. On the back edge of the furnace-bottom is placed a prism of cast iron called a *back-stone*, six and a half inches square and twenty-eight inches in length; on this rests the nozzle of the tuyere, over which is again placed another cast iron prism called the *pipe-stone*, of the same length as the back-stone, and eight inches in height. This has at the centre a cavity for the introduction of the tuyere, and projects about two inches over the cavity of the hearth; on it is again placed another back-stone of the same dimensions as the first, which completes this side of the hearth, and makes its total height from the sole



200.

plate twenty-five and a half inches. Along the two lateral edges of the hearth-bottom are placed two prismatic castings called *bearers*; these are twenty-six inches in length and five inches square, and consequently project slightly over the upper edge of the work-stone. At the height of five inches above these bearers, and at a distance of twelve inches from the back of the hearth, is supported another bar of cast iron, called the *fore-stone*, which rests on fire-bricks, and has the same form and dimensions as that on which rests the tuyere of the blowing apparatus. The space at each end of the fore-stone is now closed by a cube of cast iron measuring six inches of a side, called a *key-stone*; two others, of similar dimensions, are used for making good the space between the fore-stone and the back part of the furnace.

Before the work-stone, a, and set in masonry enclosed in a circular cast iron jacket, G, is situated the lead pot, E, into which the melted metal, as it issues from the hearth, is conducted by the

oblique channel, f, sunk beneath the surface of the iron plate. In the woodcut this pot has not been placed sufficiently near the furnace. To prevent the escape of fumes into the smelting-house, which would seriously injure the health of the persons employed, the entire hearth is enclosed in a hood of arched masonry,  $\mathbf{H}$ , communicating with the chimney, and in which is left a small door,  $\mathbf{I}$ , for the introduction of the ore and fuel. The moveable iron plate, k, admits of being raised or depressed at pleasure, according to the degree of draught required; and the blast communicating with the tuyere is regulated by a valve placed in a pipe approached by the arched door-way,  $\mathbf{L}$ , which is left open for this purpose. The brick-work is consolidated and bound together by the heavy iron straps, l, kept in their places by screw-bolts passing through the masonry beneath the foundation of the hearth.

Treatment of Ores in the Scotch Furnace: Roasting .-- The ores smelted in the Scotch furnace were, to within a comparatively recent period, merely subjected to a careful mechanical preparation, previous to their direct metallurgic treatment. It has, however, of late years been found advantageous to roast them, so as to effect their partial desulphuration and oxidation, before working them for the metal they contain. The furnace employed for this purpose varies considerably in its dimensions in order to suit the different varieties of mineral operated on, but always consists of a long flat hearth, covered by a low arch, and heated by a fireplace situated at one end; there are also, in most cases, two doors, on either side, for the withdrawal and working of the mineral treated. From nine to eleven hundred weight of galena or other ore of lead usually constitutes the charge of a furnace of this description, and requires from two and a half to three hours to become sufficiently roasted. The mineral, which is introduced into the furnace without any kind of flux, is first spread evenly over the surface of the sole, and the fire afterwards so arranged as to keep it constantly at a temperature below the melting point of galena. By this means copious fumes of sulphurous acid are presently seen to escape from its surface, and if any portion should, from approaching too nearly the point of fusion, become clammy, a fresh surface is presented to the action of the air. In this way a large proportion of the sulphur, arsenic, &c., contained in the mineral is driven off, and the slime ores and other friable substances are so far agglutinated as to be enabled to resist the force of the blast without being liable to be carried off into the flues in the form of fine dust.

Smelting.—At the termination of every shift, a quantity of ore remains on the hearth in a semi-reduced state, called *browse*, and is more or less mixed with fragments of coke and clinkers, from which it is afterwards roughly separated.

To commence a new shift, the cavity of the furnace is filled up with peat cut into rectangular blocks : those at the back part of the hearth are heaped up without any kind of order, but those placed towards the front are arranged in the shape of a regular wall. The bellows is now set in action, and an ignited peat thrown immediately before the nozzle, which guickly communicates the combustion to the whole mass. On the top of this a few shovelfuls of coal are afterwards sprinkled, for the double purpose of binding and consolidating the mass, and also to increase the temperature obtained. The browse resulting from the preceding operation is then thrown on the surface of the ignited mass, and shortly afterwards the larger portion of the matters contained in the internal basin of the hearth, are, by the aid of a large rake, drawn out on the work-stone; the refuse, or grey slag, which is known by its shining appearance, is now removed with a shovel, and thrown to the right of the furnace. The browse thus cleaned from slag is again thrown back into the hearth with the addition, if it be required, of a little finely powdered coal. If, as sometimes happens, the browse has not been properly freed from slag, but becomes pasty, and evinces a tendency to fuse, it must be hardened by the addition of a small quantity of quick-lime, which, by its affinity for the siliceous and other matters present, dries up the materials in such a way as to facilitate the subsequent extraction of the lead. When, on the contrary, the ore is found too refractory, a small addition of lime is made; but in this case a less quantity is employed, as it is only intended as a flux for the refractory matters present, and not, as in the other instances, to act also as a dryer of the too fusible scoriæ obtained. The lumps of slag which are thus formed contain on an average one-tenth part of the lead originally present in the ore, and are therefore collected for the purpose of being afterwards treated in a small cupola-furnace called a slag-hearth.

When the whole of the browse has been thrown back into the hearth, a few shovelfuls of roasted ore are sparingly thrown on the top of it: before doing this, however, it is necessary to remove the scoriæ, and place a lump of peat before the tuyere, which not only prevents any of the mineral from entering the nozzle, but likewise, from its porosity and the readiness with which it is ignited, serves to spread the blast equally through the different parts of the mass. After an interval of about twenty minutes, the contents of the furnace are again drawn out on the work-stone, and another portion of metallic lead is carried by the channel, f, into the pan, E. The grey slag is removed by the use of the

rake, and another lump of peat is placed below the tuyere. The browse, together with a proper quantity of coal and quicklime, are again thrown on the fire, and on the top of the whole is laid a fresh supply of raw or roasted ore. These operations are continued during twelve or fourteen hours, and at the termination of the shift a produce, varying with the nature of the ore, of from one to two and a half tons of metallic lead is obtained.

The lead prepared by this process is invariably more pure than that produced in the smelting furnace: this arises from the circumstance, that, being exposed to a less elevated temperature, the more fusible constituents of the ore are alone obtained, whilst in the smelting furnace the heat employed is so great as to effect the reduction of some of the foreign metals contained in the mineral, which, by entering into combination with the liberated lead, tend to impair its quality.

**Slag Hearth.**—The various slags obtained from the different operations of a lead-smelting works are divided into two classes. Those which contain so small a proportion of metal that its extraction cannot be conducted with advantage are thrown away; whilst those in which the amount of lead is sufficiently considerable are treated in the *slag-hearth*.

This consists of a blast furnace—fourneau à manche—having the form of a rectangular prism, about twenty-six inches in length, twenty-two in breadth, and thirty-three in height. The bottom is composed of a cast iron plate two inches in thickness, which is laid with a slight inclination from the side of the tuyere towards the front of the furnace. On each side of the bottom plate are placed cast iron bearers, similar to those of the ore-hearth already described; and on these is supported the fore hearth, which consists of two stout plates of cast iron, of about twelve inches in breadth and twenty-six in length. A space of about five inches is thus left between these front stones and the bottom of the furnace, and an additional height of two and a half inches is gained by placing between them a row of fire-bricks laid on their flat.

The slags which escape from this furnace through the opening at the breast pass over the surface of a pot of peculiar construction, and then flow into a large iron cistern sunk into the earth, and through which a current of cold water is constantly made to flow. This causes the liquid slags to fly in pieces, and thus adapts them for the operation of washing, to which they are subsequently subjected.

Before working a furnace of this description, its bottom is filled, to the height of about fifteen inches, with small spongy cinders pretty closely beaten together, and which reach to within four or five inches of the orifice of the tuyere. The pot for the reception of the lead is likewise filled with these cinders, which are in both cases intended to act the part of a filter in the separation of the metallic lead from the less fusible contents of the hearth. On the filter of cinders thus prepared are piled masses of peat, similar to those used in the Scotch furnace: one of these is ignited and thrown before the tuyere, and the blast immediately turned on.

When the peat has become fairly ignited, some good hard coke is thrown in, and, as soon as it appears properly inflamed, a stratum of grey slag, or any other product to be treated, is introduced. The hearth is from this time supplied with alternate strata of fuel and slag, as explained under the article Iron, when describing the reduction of iron ores. In this process metallic lead and a perfectly fluid slag are obtained; but the former is entirely separated from the latter by percolating through the ashy filter, whilst the slag, from its viscidity, can only flow over its surface. When the slag has become sufficiently melted, which happens shortly after the furnace has been first set in action, the workman with a bent iron bar makes a hole of about an inch in diameter directly through the layer of cinder: this causes the liquid silicates to flow out of the furnace in a red hot stream, which, after passing over the surface of the pot for the reception of the lead, falls into the large cistern of water. The lead obtained from the slag hearth is, from the high temperature at which it is reduced, always inferior in quality to that procured directly from the ore, and this process, therefore, is never applied to the treatment of products which admit of being economically worked by either of the furnaces before described.

. In addition to being employed for the reduction of slags and other lead products affording but a small per-centage of that metal, this apparatus is sometimes applied to the smelting of some of the foreign carbonates of lead, in the elaboration of which the object sought is rather the extraction of the silver which they contain than the reduction of the largest possible amount of lead.

From the facility with which lead becomes sublimed at high temperatures, large quantities are in all smelting establishments annually carried off in the form of fume.

This not only causes considerable loss to the smelter, but is likewise extremely prejudicial to the vegetation and cattle in the neighbourhood of the works, and for this reason every precaution is taken to prevent its dispersion in the atmosphere. With this view the flues connected with the various furnaces are commonly made to communicate with large chambers, in which the sublimed lead is condensed by a shower of cold water falling from the roof. With the same view, the whole of the gases passing through the flues have been sometimes drawn through a stratum of cold water; but all these contrivances, from the amount of mechanical power required to work them, are costly in their operation, and for this reason, long flues, in connection with properly-constructed condensing chambers and a high chimney, are more generally preferred. The condensed fumes obtained from the flues are best treated by being first roasted with a mixture of raw ore, and afterwards smelted in the Scotch furnace.

Castillian Furnace .--- Within the last few years a small blast furnace has been introduced into the lead works of this country which will, in all probability, not only entirely supersede the slag hearth, but be also extensively applied to the fusion of the more refractory varieties of lead and silver ores. This furnace is circular, usually about three feet in diameter, and is constructed of the best fire-brick, so moulded as to fit together, and allow all the various joints to follow the radii of the circle described by the brick-work. Its usual height is about 8 feet 6 inches, and the thickness of the masonry is invariably 9 inches. In this arrangement the breast is formed by a semicircular iron pan, furnished with a lip for running off the slag, and a longitudinal slit for the convenience of tapping. On the top of this cylinder of brickwork a box-shaped covering of masonry is supported by a castiron framing resting on four pillars, and in this is placed the door for the purpose of feeding, and the outlet by which the various products of combustion escape into the flues. The lower part of this hood is fitted closely to the body of the furnace, whilst its top is closed by an arch of 41 inch brick-work laid in fire-clay. The bottom consists of a mixture of fire-clay and coke-dust slightly moistened and well beaten in to the height of the top of the breast-pan, which may be nearly three feet above the level of the floor. Above the breast-pan an arch is so turned that, when the breast has been built up, it may form a sort of niche 18 inches in width, and rather more than two feet in height. When the bottom has been properly beaten in, up to the required height, it is hollowed out so as to form an internal cavity communicating freely with that of the breast-pan, which is likewise filled with brasque, and subsequently hollowed out to the depth of the internal basin of the furnace. The blast is applied to this arrangement by means of three water tuyeres, three inches in diameter at the smaller end, and five and a half inches at the other extremity, into which the nozzle is introduced. The air is generally obtained by means of a ventilator, and is conveyed to the tuyeres through brick channels formed beneath the floor of the establishment in which the furnace is situated.

The ores or other plumbiferous matters treated in this appa-

ratus ought never to contain above 30 per cent. of lead, and if richer, should be reduced to this tenure by the addition of a proper amount of poor slags. In charging this furnace it is of the greatest importance that the coke should be thrown in the middle, whilst the matters to be treated are spread around next the brick-work; by this means the furnace is prevented from becoming too hot, and the bricks consequently preserve for a much longer period.

For the purpose of allowing the slags which are produced to escape into the breast-pan, a brick is left out of the front of the furnace at the height of the fire-hearth, which, for the purpose of preventing the cooling of the scoriæ, is constantly kept covered by a layer of coke-dust or cinders. From the breast-pan the slags flow constantly out through a spout made for that purpose into east iron waggons, where they consolidate into masses, having the form of truncated pyramids, of which the larger base is about two feet square. When a sufficient amount of lead has accumulated in the bottom of the furnace, it is let off into a lateral leadpot by removing a plug of clay from the top hole situated in one of the slits of the breast-plate, and after being properly skimmed is laded into moulds.

The waggons into which the liquid slag is run off traverse over a small railroad provided with turn-tables, and other appliances by which when one mass has been removed, its place may be readily supplied by another. When cold, the casings of the waggons are turned over, and the blocks of slag readily removed. One of the great advantages obtained by this method of manipulation arises from the circumstance that, should the furnace at any time run lead or matt without its being observed by the smelter, the whole of it will collect at the bottom of the waggon, where the block obtained is considerably contracted, and from which any metallic substances are removed when the mass has become sufficiently cool.

These furnaces are found to smelt rich slags and other plumbiferous matters, with an expenditure of about 10 per cent. of coke, whilst the scoriæ obtained from them ought, in no instance, to contain above 1 per cent. of lead.

In working this arrangement, care should be taken to prevent too much flame from appearing at the tunnel head, since, provided the slags are liquid and flow readily off, the cooler the furnace can be kept the less will be the loss of lead through volatilisation. In addition to the greatest attention being paid to the working of the furnace, it is also necessary, in order to obtain the best results, that every establishment in which this apparatus is employed should be provided with capacious and extensive flues, in which the condensation of the fume takes place before arriving at

## GERMAN METHOD OF LEAD-SMELTING.

the stack through which the more volatile matters make their escape. As an instance of the perfection to which smelting with these furnaces has been brought, it may be stated, that slags giving by assay 8 per cent. of lead, and traces of silver of no commercial value, are now treated with very great advantage. In Derbyshire, where large heaps of slag of the above per-centage have recently been treated by the Castillian furnace,  $3\frac{1}{2}$  per cent. only was directly obtained from the furnace in the metallic form, whilst above 4 per cent of lead was obtained from the flues in the state of fume, and subsequently reduced in a reverberatory furnace, so that the results yielded in practice are just equal to those indicated by assay.

## GERMAN METHOD OF LEAD-SMELTING.

In some parts of Europe, and particularly where the ores have a low produce in lead, and are at the same time associated with a siliceous gangue, the metal is reduced by the action of metallic iron in the way described when treating of lead assaying.

If minerals of this class were subjected to similar processes to those employed in this country for moderately rich galenas, a large quantity of lead would be lost in the form of oxide, which, instead of reacting on the undecomposed sulphide, would combine with the silica present to form a vitreous slag extremely difficult of reduction. The method of reducing the sulphide of lead by means of metallic iron is extensively practised in many parts of the Hartz, particularly at Clausthal.

The ore treated consists of a mixture of crushed galena and schlich, to which are added various secondary products obtained at different stages of the process.

The mixture treated in the furnaces of Clausthal consists of 34 quintals (cwts.) of ground ore and schlich, equivalent to 24 quintals of pure galena.

4 to 5 quintals of cupel bottoms strongly impregnated with litharge.

1 quintal of abstrich or first oxide formed on the surface of the cupel.

39 quintals of slags, derived either from the first fusion of the mineral treated, or from the remelting of the matts. These slags are added for the purpose of effecting the fusion of the gangue.

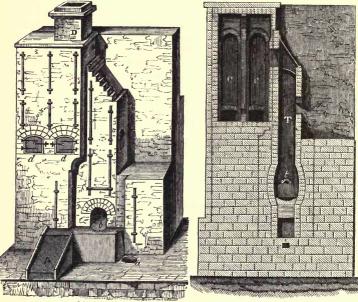
41 quintals of granulated cast iron.1

The fusion of this mixture is conducted in a small blast furnace of from twenty to twenty-five feet in height, and about three feet in diameter in the widest part. The crucible placed at the bottom

<sup>1</sup> Regnault.

of the hearth is so arranged as to extend beyond the breast of the furnace into a small raised platform situated immediately before it. The lining of the hearth consists of a kind of refractory firestone, and the bottom, which is slightly hollowed, is covered for a considerable thickness with a mixture of powdered charcoal and refractory clay, in such a way as to afford a gentle slope from the side of the tuyere to beyond the front wall of the furnace. A tapping-hole enters at the lowest part of this basin, and affords a means of drawing off its contents when accumulated in sufficient quantity.

This receiving basin, a, fig. 201, is placed on a level with the floor and at some distance from the breast of the furnace, which is supplied with a current of air forced through two tuyeres situated at t, fig. 202, in the opposite face of its refractory lining. In charging the mineral, care is taken to direct it towards the



201.

202.

side of the tuyere, whilst the combustible is chiefly thrown towards the breast. The cold air constantly entering these tuyeres rapidly cools the slag produced in their immediate vicinity, and forms around the nozzles circular channels of six or seven inches in length, on the proper management of which in a great measure depends the success of the operation. One of the principal effects produced by these channels is to prevent the oxidation of the ore, as the blast is by this means brought into immediate contact with the fuel without having to pass through the mineral charged at the back of the furnace, and cannot therefore, so readily give rise to the formation of litharge and the consequent loss in the form of fusible silicates of lead.

With this view the smelter bestows the greatest attention to the proper regulation of the length of the slag nozzles, as by it the economical working of the furnace is most materially affected. It is also found necessary, by a proper regulation of the supply of air and fuel, to so arrange the temperature that the upper extremity of the shaft may not become too strongly heated, as in this case large quantities of galena are driven off before arriving in that part of the furnace in which their decomposition is effected. With all these precautions, there is, however, a constant loss from sublimation, and therefore the whole of the gases passing from the tunnel-hole, **T**, are made to pass through a series of chambers, c c, before escaping into the atmosphere by the chimney, **D**.

In these chambers large quantities of fume gradually accumulate; this is occasionally removed through the doors, d, for the purpose of being mixed with other lead products, and again treated in the furnace.

During the whole time this arrangement is in action the scorize flow continuously into the fore-hearth, where, being solidified, they are seized by a labourer with a stout iron hook, and dragged down the inclined plane, p, to the foundry floor. When the interior basin, b, has become filled with metallic products, the plug is removed from the tapping-hole communicating with the reservoir, a, into which the fused metal is rapidly drawn off.

The products thus run off into the outer basin readily divide into two parts; the lower portion is metallic lead, whilst the higher consists of sulphide of lead more or less mixed with the sulphide of the other metals originally present in the ore, and particularly with sulphide of iron resulting from the decomposition of galena by that metal. This substance, which readily solidifies, is called the *first lead matt*, and is removed from the surface of the bath by an iron hook, and stowed in a proper situation for subsequent treatment. The lead is afterwards laded into moulds, where it assumes the form of massive lenticular ingots. The poorer slags are now removed and thrown away, whilst those which have been withdrawn from the surface of the external basin, and contain numerous granules of metallic lead, are added as a flux in a future operation. When a sufficient quantity of rich slag is not to be procured, some of the poorer scoriæ are likewise used for this purpose; but this never takes place, except when a proper supply of the richer variety is not to be procured. The products obtained from a mixture having the weight and composition before given, consist of nineteen quintals of metallic lead and eight quintals of first matt, containing from 30 to 35 per cent. of lead.

When a sufficient quantity of these first matts have accumulated in the establishment, they are roasted in heaps, laid on a stratum of fuel, and by this means large quantities of sulphur and sulphurous acid are disengaged.

This first roasting occupies from three to four weeks, at the expiration of which time the heap is carefully picked over and the products divided into two classes; those portions which have been sufficiently roasted are again taken to the furnace and retreated, whilst those fragments which still retain a considerable amount of sulphur are subjected to a second process of roasting. In this way four successive roastings are necessary before the whole of the matt is obtained in a fit state for metallurgic treatment.

When sufficiently roasted, the matts are fused in a small blast furnace, after being mixed in the following proportions with various other bodies :---

32	quintals	of roasted matt.
30	- ,,	of rich slags obtained from the direct treatment
		of the ore.
4 to 5	22	of cupel bottoms.
2	22	of abstrich or first oxides obtained from the cupel.
2		of slags from the reducing furnace.
1	,,	of granulated cast iron.

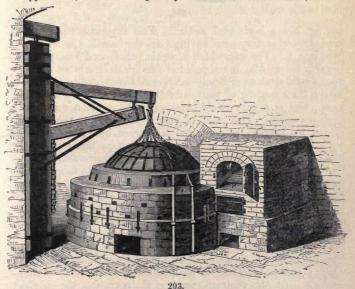
The furnace in which this mixture is now introduced is about five feet in height and considerably contracted in the vicinity of the crucible, which, as in the case of the larger apparatus, is provided with a sloping fore-hearth and a distinct tapping-basin for the reception of the metallic matters produced.

The combustible employed is coke, and the blast, which is supplied by a single tuyere, is conducted into the furnace through a slag nozzle of about three inches in length. During the process of roasting, the larger proportion of the sulphide of iron passes to the state of oxide, and during the subsequent fusion, this oxide, which is partially reduced by the carbon of the fuel, becomes protoxide, and unites with the siliceous matters present to form a vitreous and extremely fusible slag, which flows through the aperture of the fore-hearth, and is continually removed. The sulphide of lead is at the same time reduced through the agency of the metallic iron, and a new matt, analogous in its composition to the first, is obtained.

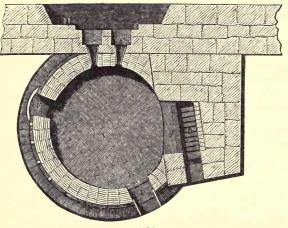
These matts, when sufficiently solidified by cooling, are removed in the way already described, after which the lead is taken out in large iron ladles and cast into circular pigs.

The treatment of thirty-two quintals of roasted matt, with its associated fluxes and other products, affords twelve quintals of metallic lead and eight quintals of *second matt*.

The second matts are subjected to a similar treatment to that employed for the reduction of those obtained by the direct treatment of the ores. They are first made to undergo three or four successive roastings, and subsequently treated in the same furnace and with the same additions as are employed in the case of the first matts. In this way a further amount of metallic lead and a *third matt* is obtained; this is again roasted, fused with a proper addition of fluxes and other matters, and metallic lead and a *fourth matt* is the result. The copper, of which a small quantity only is contained in the original ore, having a greater affinity for sulphur than is possessed by lead, continually accumulates in the matts, which, after the fourth roasting and fusion, become extremely rich in that metal. The sulphide last obtained is known by the name of copper matt, and is subsequently treated for that metal.



The lead obtained by these different processes often contains a sufficient amount of silver to render its extraction a matter of considerable commercial importance, and it is then subjected to direct cupellation in a furnace, of which fig. 203 represents a back view,



204.

and fig. 204 a horizontal section. This apparatus consists of a kind of reverberatory oven, having a circular hearth, A, and a lateral fire-place, B. The sole, which is regularly hollowed from the sides towards the middle, is composed of fire-bricks closely set on edge upon a solid stratum of firmly compressed scoriae, and again covered with a thick coating of marl carefully beaten down by iron rammers; this is always relaid previous to the commencement of a fresh operation. This layer of marl corresponds to the test employed by English refiners, and is covered by a dome of brickwork bound with iron, and capable of being either removed or lifted into its place by means of a number of chains attached to a lever supported by the moveable crane, c. In the sides of this furnace are five openings; by the largest of these, d, the flame passes from the fire-place into the interior of the hearth; the two openings, t t', serve for the introduction of the tuyeres, by which a current of air is thrown on the fused metal, both for the purpose of assisting in its oxidation, and forcing, at the same time, the litharge formed on its surface towards the aperture, E, from which it escapes in the fused state; finally, the opening F, through which is inserted the lead to be operated on in the form of circular discs. At the commencement of the operation, the opening,

E, is entirely closed by the marl of the cupel; but in proportion as the operation advances, the gateway is successively cut down by a pointed iron bar to the level of the litharge contained in the furnace. The litharge which escapes from this opening flows down to the floor of the building, where it is allowed to accumulate.

Before commencing a cupellation it is necessary to arrange the cupel, and for this purpose, after having removed the dome, the old cupel bottom, strongly impregnated with litharge, is broken up and carried away to be treated for the lead it is capable of affording. The brick bottom is now moistened with water, and covered by a thick layer of marl, well consolidated by the use of a heavy iron rammer; the covering is afterwards replaced, and firmly luted in all its joints with a little stiff fire-clay. When this has been done, the furnace is charged with 160 quintals of lead, and the fire immediately lighted. The lead soon begins to melt, and immediately that the whole of it has become fused the bellows are set slowly in action, and rapid oxidation begins to take place. The metallic bath at first becomes covered by a blackish pulverulent substance consisting of a mixture of oxide of lead and the various foreign bodies present. These matters, from the low temperature at which the operation is conducted, do not become fused, and the workman, after throwing on the surface of the bath a few shovelfuls of charcoal dust, proceeds to the removal of the abstrich, by means of a block of wood placed transversely at the extremity of a long iron rod, and by which he gently draws it through the litharge-hole and out of the furnace. At the expiration of a short period a fusible litharge begins to make its appearance; but that at first produced is extremely impure, and therefore not mixed with that obtained at a later period of the operation. At length a purer oxide, commercial litharge, begins to be formed, and the blast is at this point progressively increased for the purpose of augmenting the rapidity of oxidation. The nozzles of the tuyeres supplying air to the cupel are frequently covered by small valves, called butterflies, which, from their weight, serve to spread the blast over the whole surface of the metallic bath. The operation is thus continued until the whole of the lead has been removed in the form of litharge, and a plate of nearly pure silver remains at the bottom of the cupel.

Immediately after the brightening has taken place, the workman throws water over the surface of the metallic residue; for this purpose hot water is at first employed, but when the plate of silver begins to be solidified, cold water is used. The residual metal, which is not yet absolutely pure, but contains about 1-16th of lead, is now removed from the furnace, for the purpose of being refined by a process which will be described when treating of silver.

The time necessary to make a cupellation of the amount of lead above stated, including the preparation of the fuel, is generally about 30 hours. Wood is the combustible employed for heating this furnace.

At Clausthal, the cupellation of 160 quintals of lead, obtained from the first fusion of the ore, usually yields 56 marks of silver, and that obtained from the roasted matts, which is somewhat richer, affords on an average 62 marks of that metal.<sup>1</sup> The last portions of litharge which are obtained, contain a notable amount of silver, and for this reason are not mixed with that produced during the former stages of the operation. The litharge produced, with the exception of small quantities, which are sometimes sold for various purposes, is again reduced to the metallic state. This reduction is effected in a small blast furnace, with an exterior basin into which the metallic lead is tapped, and the slags produced during the operation are added to raw lead ores, with which they are afterwards treated. The metallic lead obtained is subsequently cast into rectangular ingots, in which form it becomes an article of commerce.

Method of Pontgibaud.—The treatment of lead ores formerly employed at Pontgibaud, in the vicinity of Clermont (Puy de Dôme), was peculiar to this establishment, and had been adopted in consequence of the exceptional composition of the ores operated on, and the high price of fuel in the district. The mineral, when brought to the surface, is generally poor for lead, but contains a considerable amount of silver, and is consequently subjected to a careful mechanical preparation. This concentration of the ore cannot, it is stated, be carried beyond a certain limit, as the lighter substances thrown away as sterile are found to contain a considerable quantity of silver, and the washing is therefore only carried so far as to allow of the ores being successfully subjected to metallurgic treatment.

The largest proportion of the ore reaches the foundry in the form of finely-divided sand or schlich, which, from the large amount of siliceous matters which it contains, does not admit of being smelted in the ordinary reverberatory furnace, and which on the other hand, is, from its fine state of division, unfit for immediate treatment in the low blast furnace of the Hartz.

Before being treated for metallic lead, these ores were roasted in a reverberatory furnace, having an extremely long hearth, and of which two were arranged one above the other. On the first of these the mineral was roasted, whilst on that placed nearest the fire-bridge they were agglomerated into masses, suitable for subsequent treatment in the ordinary low continental furnace. This second fusion for metallic lead was conducted as in the Hartz, with the addition of metallic iron, and various other fluxes. The following mixture is that with which the furnace was ordinarily charged :---

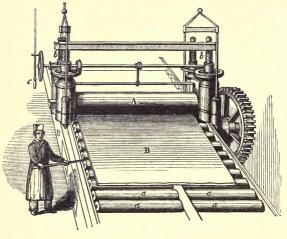
Roasted ore,	1,000 1	rils.1
Fluoride of calcium,	100	22
Carbonate of lime,	240	22
Old iron (in small fragments),	100	>>
Cupel bottoms, abstrich sweepings from		
furnaces, &c.,	60	"
Rich slags from furnace operations, . 500 t	io 600	,,

This was thrown into the furnace alternately with suitable quantities of hard coke. When in a good working state, each furnace was capable of running down three times the above amount in the course of 24 hours, and when the preliminary roasting had been carefully performed, no matt was obtained, but merely metallic lead, together with a fusible and liquid slag. The cupellation of the rich lead was performed in the ordinary German refinery, with a bottom 9 feet in diameter, covered by a floor composed of 1,400 kils. of calcareous marl, 280 kils. of slaked lime, and the same quantity of well-mixed clay. As in the various German establishments, the plate of silver obtained was afterwards subjected to a second treatment, by which the last traces of combined lead were removed.

The management of this establishment has, however, been recently transferred to the Messrs. Taylor, of Queen-street Place, London, by whom all the more modern improvements employed in this country have been introduced with the greatest success.

### LEAD MANUFACTURE.

This metal is chiefly employed in the arts, either in the form of sheets for covering houses, making gutters, &c., or for the manufacture of pipes for the conveyance of water and other liquids. In order to make lead into sheets, it is first moulded in a cast iron frame into the form of a plate, from six to seven feet square, and six inches in thickness. When this has sufficiently cooled, it is lifted from its mould by a powerful crane, and placed on the machine by which it is to be rolled out into sheets. This consists of a long frame or bench, fig. 205, three feet in height, eight feet in width, and from seventy to eighty feet in length. At intervals of every foot are placed the rollers, *a a*, &c.,



205.

all on exactly the same level, and so arranged that a heavy body may be pushed from one end of the frame to the other with the greatest facility. In the centre of this stage is the rolling machine, consisting of two heavy rollers, of which only the upper one, A, is seen in the woodcut, and which, by powerful machinery, are made to revolve in contrary directions : each of these cylinders is sixteen inches in diameter, and is turned perfectly smooth and level on the surface. By means of the screws, b, and the connected pinion wheels, the distance between these may be regulated with the greatest accuracy on turning the disc, c, which for this purpose is furnished with a graduated plate and pointer.

The motion of the rollers also admits of being readily reversed by a very simple mechanical arrangement. The plate of lead thus prepared is afterwards brought between the rollers, by which it is strongly compressed, and gradually drawn through to the other side, when the distance between them is diminished, and by reversing the motion of the mill, the sheet is again drawn back to the part of the platform on which the original plate was first laid. This process is repeated a great number of times, the plate, B, first passing from the left to the right, and then from right to left, until its thickness has been very considerably reduced. The motion of the leaden plate is much facilitated by the small wooden rollers, a a, and when the length obtained by the reduction of its thickness becomes inconveniently great, it is divided into two parts, and each half milled in a similar manner.

The lead is in this way sometimes passed between the rollers from two to three hundred times; its thickness being diminished, and its length increased, by each successive operation. The original plate is by this treatment generally extended into a sheet, which, when intended for roofing purposes, is about 400 feet in length, and 7 feet in breadth. This is afterwards cut up into convenient lengths, and rolled up for the use of the plumber, whose business it is to adapt it to the various purposes to which sheet lead is applied.

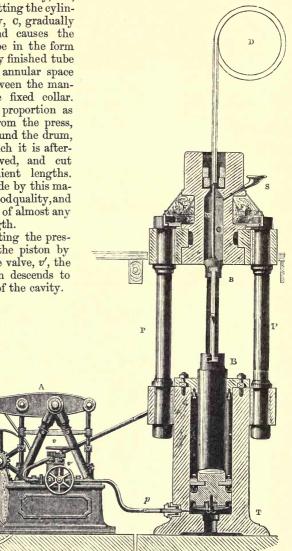
The manufacture of lead pipe by the ordinary method, combines, like that of sheet lead, the double process of casting and elongation. Whatever may be the dimensions of the pipe required, it is first cast in the form of a short and extremely thick cylinder, which is afterwards reduced to the proper size by being forcibly drawn, when placed in a mandril of the exact size of its proposed. internal diameter, through a succession of progressively decreasing steel dies. By this process, however, although affording pipes of good quality with regard to soundness and finish, lengths of from 20 to 30 feet only can be obtained, and, consequently, when very long pieces without a joint are required, recourse must be had to the hydraulic pipe-press, fig. 206. This machine consists of a common hydraulic press, T, connected with a double force pump, A, by which water is pumped beneath the piston, B, through the small metallic pipe, p; above the top of the press and on a level with the floor of the workshop, is supported by the stout iron pillars, P, a heavy casting, containing the cylindrical reservoir, c, for the reception of the metallic lead, and an annular fire-place, F, charged with pit coal, and communicating with a chimney for the escape of the smoke. At the upper extremity of the cavity, c, is secured a steel die, of the diameter of the outside of the pipe to be made, whilst a mandril, m, which passes directly through its centre has the same dimensions as the inside of the pipe which is to be produced.

To use this apparatus, the piston, B, is brought into the position shown in the woodcut, and the space, c, filled with molten lead, through the spout, s, which is immediately removed, and the aperture firmly stopped by a stout iron plug, kept in its place by a strong key. The pressure is now established by admitting

the other extremity, B', accurately fitting the cylindrical cavity, c, gradually upwards, and causes the lead to escape in the form of a perfectly finished tube through the annular space existing between the mandril and the fixed collar. The pipe, in proportion as it escapes from the press, is coiled around the drum, D, from which it is afterwards removed, and cut into convenient lengths. The pipe made by this machine is of good quality, and may be made of almost any required length.

On admitting the pressure above the piston by means of the valve, v', the plunger again descends to the bottom of the cavity.

the water through the valve, v, beneath the piston, which forces



206.

Several alloys of lead with other metals are employed in the arts, but by far the most important of these are type metal, and the various mixtures of lead and tin known by the name of solder. Plumber solder is a compound of two parts of lead and one of tin; the solder used in the manufacture of articles in tin-plate is an alloy of these metals united in equal proportions. The composition of type metal has been described when treating of antimony.

a state by sent the south in the state of the

# SILVER.

# Equiv. = 108. Density = 10.47.

SILVER is the whitest of all the metals, and is capable of receiving a lustre inferior only to that of polished steel. Its malleability and ductility are, next to gold, greater than that of any other metal. When pure, it is so soft as to be readily cut with a knife, and in that state enters into fusion at a full red heat, corresponding, according to Daniell, to 1873° of Fahr. scale. When fused in open vessels, it absorbs oxygen in considerable quantities, sometimes amounting to 22 times the volume of the metal itself. On becoming solid, however, the whole of this gas is again expelled; and, to this circumstance is probably, in some degree, owing the metallic vegetation which takes place on the surface of silver buttons, when suddenly cooled on the cupel. When silver is heated to redness in contact with porcelain or glass, the absorbed oxygen combines with the metal to form an oxide, which, uniting with the silicic acid of the substance with which it is in contact, gives rise to the formation of a yellow enamel. When heated very strongly in a blast furnace, this metal gives off sensible metallic vapours, and if exposed to the high temperature between two charcoal electrodes in connection with a powerful voltaic battery, is readily By fusing a large quantity of silver, and afterwards volatilised. allowing it to cool very gradually, cubic and octahedral crystals may, on piercing the solidified crust and running off the still liquid metal, be obtained. When solutions of silver are decomposed by the action of feeble electric currents, the precipitated metal is frequently found to assume a crystalline form. This metal does not absorb oxygen at ordinary temperatures, but speedily becomes blackened on exposure to an atmosphere containing the most minute traces of sulphuretted hydrogen gas, which is decomposed by it with the greatest facility.

Heated to redness in contact with the caustic alkalies, it does not become in the least affected, and is for this reason frequently employed for making crucibles to be used when attacking various substances by caustic potash. In the presence, however, of fused alkaline silicates, silver vessels to a certain extent become acted on, and the silicate is stained of a yellow colour. Oxide of silver is reduced by heat alone, and a globule of metal is thus obtained.

Unless in a state of extreme division, silver is not attacked by hydrochloric acid, and even then requires to be heated to the temperature of ebullition, before the decomposition of the acid is effected. By dilute sulphuric acid no effect is produced, but when strong sulphuric acid is employed, it is, when aided by heat, readily decomposed, with the formation of sulphate of silver and the evolution of sulphurous acid gas. Nitric acid readily attacks silver even at ordinary temperatures; binoxide of nitrogen is evolved, and nitrate of silver, *lunar caustic*, is produced. By chlorine, iodine, and bromine, silver is, even in the cold, readily attacked.

## ORES OF SILVER.

Silver occurs, in the native state, alloyed with various other metals, also mineralised by the non-metallic elements; such as, sulphur, selenium, arsenic, chlorine, bromine, iodine, and lastly, in combination with certain acids.

Besides being obtained in large quantities from lead ores, the silver of commerce is chiefly derived from Vitreous silver, Brittle or Black silver ore, Red silver, Horn silver, Malleable silver, and a natural amalgam of Silver and Mercury found extensively in some silver mines.

Native Silver; Argent natif; Gediegen Silber, is found accompanying the other ores of this metal, and more particularly the sulphide and chloride, and is frequently associated with red silver ores. It occurs either in a crystalline form, or in the state of divergent branches, of which the extremities are composed of numerous minute crystals, similar to those observed in specimens of native copper.

This metal likewise occurs in amorphous masses in long filamentary strings, and in the shape of compressed plates of greater or less extent. One of the largest masses of metallic silver ever obtained in Europe, was procured from the mines of Konigsberg, in Norway: this specimen, which is preserved at the museum of Copenhagen, weighs about five hundred pounds; others of still larger size have been cited as coming from the same locality. The crystals of native silver are seldom very perfectly defined, as they never occur in an isolated state, but in most instances impenetrate each other. The cube, the octahedron, and cubododecahedron, are among the forms which it most frequently assumes. Native silver is usually found disseminated in ferruginous rocks, as at Huelgoat in Brittany, and in the mines of Chili and Mexico, where these argentiferous iron ores receive the names of *pacos* and *colorados*. Native silver is also found in the Hartz, Saxony, Hungary and Dauphiny: large quantities are likewise afforded by the mines of Peru and Mexico, and in the United States of America some beautiful specimens of native silver have been found associated with the malleable copper, procured from the district about Lake Superior.

Native Amalgam; Argent amalgamé; Natürlich Amalgam.—This mineral, which is of a silver-white colour, and bright metallic lustre, occurs both in distinct crystals and in irregular amorphous masses; it also not unfrequently assumes the form of thin compressed plates, occupying the fissures existing between the strata.

Its specific gravity is 14.1, and when heated before the blowpipe, the mercury is expelled, and a fused button of metallic silver remains. The composition of this mercurial amalgam is, according to Klaproth—

Silver Mercury	•	•	•	•	$36 \cdot 64 \cdot$
mercury	•			•	
					$100 \cdot$

This composition would appear to correspond with the formula, AgHg<sub>2</sub>, although some other analyses indicated the presence of a larger per-centage of mercury. This mineral is found in a great many different localities, but the finest specimens have been procured from Moschellandsberg in Bavaria.

Another species of this substance forms one of the principal sources of silver in the rich mines of Arqueros, in the province of Coquimbo, Chili. From its malleability and general appearance, this compound was for a long time thought to be metallic silver. According to the analysis of Professor Domeyko, of the mining school of Coquimbo, this amalgam consists of

Silver . Mercury	•	:	•	$rac{86\cdot 50}{13\cdot 50}$
				100.00

from which it appears to be composed of six atoms of silver united to one equivalent of mercury, and its composition may therefore be represented by the formula  $Ag_{s}Hg$ .

**Vircous Sulphide of Silver**; Argent sulfuré; Silberglanz.—This mineral occurs massive, and crystallised in cubes and dodecahedrons. Its colour is a shining lead grey, and its streak, which is of the same colour, is likewise shining. The fracture of the massive varieties is slightly conchoidal, sometimes approaching to vitreous. It is fusible even in the flame of an ordinary candle, and before the blowpipe gives off sulphurous vapours, and yields a button of metallic silver. This mineral is at the same time one of the richest and most abundant ores of silver, and furnishes a large proportion of that annually produced by the various foreign mines.

It occurs in those of Saxony, Bohemia, and Hungary, and is particularly abundant in the mines of Guanaxuato and Zacatecas in Mexico. Sulphide of silver is frequently associated with the sulphides of copper, iron, and antimony.

İts composition is, according to Klaproth-

		From	Himm	elfur	st.	Fr	om	Joachimsthal.
Silver			86.5					86.39
Sulphur			13.5		•	•		13.61

100.00

# 100.0

# Brittle Silver Ore; Argent sulfuré fragile; Schwarzgiltigerz.— This mineral is of an iron-grey colour inclining to black, with a metallic lustre and unequal conchoidal fracture. It has a specific gravity of 6.2, is extremely fragile, and when broken yields a black powder.

Before the blowpipe it affords a button of metallic silver, after having given off sulphurous and antimonial fumes, in which the peculiar odour of arsenic may also frequently be detected. When crystallised, it is found in small six-sided prisms, of which the derivation has not with certainty been ascertained.

This mineral, which occurs with other ores of silver at Freyberg, Schneeberg, and Johanngeorgenstadt in Saxony, as well as in the mines of Bohemia and Hungary, and in those of Chili, Peru, and Mexico, has, according to the investigations of H. Rose and Klaproth, the following composition :---

Fro	From Freyberg.			From Schemnitz.		
B	y Klaprot	h.			By H. Rose.	
Silver	66.50				. 68.54	
Copper and Arsenic	0.20				. 0.64	
Iron	5.00					
Antimony	10.00				. 14.68	
Sulphur	12.00				. 16.42	
which they have a farmer						
	94.00				100.28	

**Polybasite** is another variety of silver ore, obtained from the Peruvian and Mexican mines. It usually occurs in tabular hexagonal prisms, and differs so little in its chemical composition from brittle sulphide of silver, as to be regarded by many mineralogists as merely another form of that mineral. Antimonial Silver is a natural alloy of these two metals, in the proportion of 16 of the former to 84 of the latter; it has a specific gravity of about 9.6, and fuses before the blowpipe into a metallic globule, from which antimonial fumes are driven off.

**Eucairite** is an argentiferous ore containing copper and selenium. This substance, which is chiefly obtained from Sweden, occurs in black metallic fibres, which, when heated before the blowpipe, afford the characteristic odour of decaying horse-radish. A mineral containing silver and silenium, together with a little lead, is likewise found in the Hartz.

Chloride of Silver; Argent corné; Hornsilber.—This mineral, which was formerly supposed to be of rare occurrence, constitutes one of the richest and most abundant ores of Chili, where it is frequently associated with native silver, apparently resulting from its decomposition. It also occurs in massive amorphous fragments in connection with sulphide of silver, but still more frequently in small cubical crystals disseminated in the ferruginous rock known in Chili and Peru under the names of pacos and collorados. The chloride of silver of Huelgoat is also of this description, and is disseminated in a cavernous hydrated oxide of iron, around the cavities of which it assumes the form of small cubo-octahedral crystals, the largest of which do not exceed in size the head of an ordinary pin.

The colour of this mineral is white or yellowish-white, which becomes violet by exposure to the air: the massive fragments when broken, present a vitreous conchoidal fracture, the edges of which are transparent, or at least translucid. Chloride of silver is extremely soft, and admits of being cut with a knife or scratched by the nail with the greatest facility. It is fusible before the flame of the blowpipe, and, when supported on a piece of charcoal, affords a white pearl-like button, which by continued exposure to the reducing flame, finally yields a globule of metallic silver. On being moistened with water, and afterwards rubbed with a piece of iron or zinc, its surface becomes covered with a film of reduced silver. Chloride of silver, when pure, consists of silver 75<sup>•</sup>3, chlorine 24<sup>•</sup>7; and its composition is therefore represented by the formula AgCl.

Specimens of this mineral, although of comparatively rare occurrence in the European mines, have been obtained from Norway, Siberia, Saxony, the Hartz, and Cornwall.

**Iodide of Silver** is a rare mineral of a pale lemon colour, with sometimes a tint of green. The colour of this natural iodide is not affected even by continued exposure to the direct action of the sun's rays, although that artificially produced in our laboratories is extremely sensitive even to diffused daylight. This mineral frequently assumes the form of minute modified cubes. It is composed of silver 77.4, iodine 22.6.

**Bromide of Silver** crystallises in minute cubo-octahedrons, which, except in their colour, which is green, very closely resemble chloride of silver. Berthier, who first examined this mineral, discovered it in the hydrated oxide of iron from Huelgoat, but it has since been so abundantly found in the district of Plataros, near Zacatecas, in Mexico, that the ores there raised have received the name of *plata verde*, from the colour imparted to them by this substance. According to the analysis of Berthier, it is composed of silver 57.70, bromine 12.50.

# ESTIMATION OF SILVER, AND ITS SEPARATION FROM OTHER METALS.

This metal is either weighed in the metallic state, as obtained by cupellation, or is precipitated from its solutions in the form of chloride, from the quantity of which the amount of silver originally present is readily deduced by calculation.<sup>1</sup>

The precipitation of the chloride is usually effected by the addition of a small excess of hydrochloric acid to the solution in which the silver is contained, and which, in order that a dense precipitate may be obtained, should be heated nearly to the boiling point previous to the addition of the precipitant : the addition of a few drops of nitric acid to the solution is also frequently found of service in obtaining a precipitate, which becomes readily deposited at the bottom of the beaker in which the operation has been conducted. When the whole of the chloride has been collected at the bottom of the vessel, the supernatant liquor is carefully drawn off into another beaker by means of a glass syphon, care being taken not to draw over at the same time any portion of the solid precipitate.

The chloride is now transferred from the beaker to a thin porcelain capsule of which the weight has been accurately taken and noted, and after being placed, for the purpose of guarding against loss, in a large porcelain dish, it is again washed with water slightly acidulated with nitric acid. When the washing has been completed, the supernatant water is drawn off by a pipette, and the crucible with its contents is removed from the porcelain dish in which it has been standing during the process, to a water-bath, in which the chloride is carefully dried. The water drawn off into the second beaker at the commencement of the operation is also

<sup>1</sup> Every 100 parts of the chloride correspond to 75.27 parts of metallic silver.

examined in order to ascertain if any deposit has taken place, and which, should any occur, must, after washing, be added to that already contained in the crucible.

When the chloride has become sufficiently dry, it is removed from the water-bath and heated over the flame of a gas-burner or spirit lamp, until it has become fused, when the crucible and its contents are again weighed; and the difference between the first and second weighings will evidently correspond to 75.27 per cent. of metallic silver. The chloride of silver, when fused, is found to attach itself so firmly to the sides of the crucible as to be extremely difficult of removal by ordinary means : it may, however, be readily detached by boiling it with small fragments of metallic zine in a little hydrochloric acid : by this treatment the chloride is reduced to the metallic state, and is then easily removed by washing.

The solubility of silver in nitric acid, and the complete insolubility of its chloride in acid solutions, render the separation of this body from the other metals in most instances an easy operation. When, however, it is present in a solution together with salts of lead and mercury, the direct addition of an excess of hydrochloric acid cannot be employed, as in this case the precipitate obtained would be contaminated by the chlorides of lead and mercury, by which the result would be seriously vitiated. When mercury alone is associated with the silver, this inconvenience may be obviated by treating the precipitate with boiling nitric acid, to which a few drops of hydrochloric acid have been added : by this means the mercury is dissolved in the state of corrosive sublimate, whilst the chloride of silver remains, on the contrary, unacted on. When lead is present, the chloride of that metal may be removed by continued washings in water containing a small quantity of hydrochloric acid. The water used for this purpose should be hot, but when the proportion of lead in comparison to that of silver is not extremely small, recourse must be had to cupellation. The separation of silver from mercury may also be effected with sufficient accuracy for metallurgic purposes by precipitating the two metals together by sulphuretted hydrogen, and afterwards roasting the sulphides in a small porcelain crucible, by which the mercury will be almost completely expelled, whilst the silver remains in the metallic state.

# ASSAY OF THE ALLOYS AND ORES OF SILVER.

Assay of Alloys.—The assay of the alloys of silver by cupellation is conducted as described when treating of the assay of argentiferous galena, except that, as many of the compounds containing silver contain other metals besides lead, and particularly copper, it becomes necessary to add on the cupel a sufficient amount of pure lead to enable the other oxides produced to sink into the bone-ash of the cupel, and thus allow the mixture to constantly present a fresh surface for further oxidation. From the circumstance that the silver money of all European nations is alloyed with copper, the mixtures of these metals are those which most frequently occupy the attention of the assayer, and the cupellation of such alloys has consequently been more particularly studied. The following directions, therefore, although especially referring to the alloys of silver and copper, are also to a great extent applicable when other metals are present in the mixture.

The amount of lead necessary to be added to an alloy of silver and copper varies in accordance with the composition of the mixture to be treated, and should be greater in proportion as the quantity of copper becomes more considerable. In making this addition it is necessary to bear in mind that the lead must be present in such quantity that the litharge formed may be enabled to dissolve the other oxides produced, and at the same time remain sufficiently liquid to be readily absorbed by the pores of the cupel. If this necessary amount be not added, the litharge formed becomes pasty, and speedily covers the surface of the cupel, which is then said to be *drowned*; whilst if too large a quantity be employed, the assay remains a long time in the fire, and a considerable loss of silver by evaporation is experienced.

The affinity exercised by the silver for copper, renders it necessary in these operations to add a larger amount of lead than would be required if pure copper alone were to be absorbed.

The following table shows, according to experiments of D'Arcet, the amount of lead necessary to effect the proper cupellation of various alloys of silver and copper.<sup>1</sup>

Standard of Silver.	Amount of Copper alloyed.	Quantity of Lead necessary.	Quantity of Lead in relation to that of Copper.
1000	0	3 t 10	
950	50	3	60 to 1
\$00	100	7	70 to 1
800	200	10	50 to 1
700	300	12	40 to 1
600	400	14	35 to 1
500	500	16 to 17	32 to 1

Berthier, Vol. II. p. 851.

<sup>+</sup> Even with pure silver it is found necessary to add a little lead on the cupel, as the button would not otherwise assume the rounded form which is required.

Standard of Silver.	Amount of Copper alloyed.	Quantity of Lead necessary.	Quantity of Lead. in relation to that of Copper.
400	600	16 to 17	27 to 1
300	700	16 to 17	23  to  1
200	800	16 to 17	20 to $1$
100	900	16 to 17	18  to  1
Pure copp	per 1000	16 to 17	16 to 1

It will be remarked, that below the standard of 500, or onehalf silver, the proportion of lead to be employed constantly remains the same, whatever may be the constitution of the alloy; this fact is fully borne out by experiment.

As a general rule, it is found that a cupel is capable of absorbing its own weight of litharge, and consequently, when the composition of an alloy is nearly known, it becomes easy to choose a cupel of the right size for conducting the operation. It is likewise of importance that the lead employed for the assay should contain but a very small proportion of silver, and it is evidently essential that in all cases the assayer should be assured of the exact quantity of this metal by means of repeated trials. The lead added to the alloy being in all cases weighed, its corresponding amount of silver must be deducted from that obtained from the alloy at the termination of the experiment.

The results of the operation are also considerably influenced by the temperature at which the cupellation has been conducted, and consequently all assays made in this way are liable to a certain amount of error. When the muffle is too strongly heated, the silver becomes perfectly refined, but experiences a loss through sublimation and absorption by the cupel; whilst, on the contrary, when the temperature has not been sufficiently elevated, the button is not thoroughly refined, but retains a portion of lead. These two causes of error, existing at the same time in all cupellations, are found in practice to almost neutralise each other, although it is necessary to employ various minute precautions in order to obtain satisfactory results.

The assayer should, in the first place, constantly heat his furnace to the same temperature, and make a table of corrections by which he may be enabled for each alloy to determine the addition which should be made to the result found, in order to arrive at the correct standard of the mixture. This table is constructed by cupelling a series of alloys made by melting together proper mixtures of copper and silver, and of which the true composition is consequentlyknown. This table can, however, be only employed by the assayer who constructs it, as it is merely applicable to the particular furnace in which the standard cupellations have been made. For the purpose of checking the results incorporated in the table, it is also prudent to make from time to time an assay on an alloy corresponding to one of those first operated on, as by this means it is easy to discover whether the loss during the cupellation remains constant for each alloy, and consequently whether the tabular corrections may still be safely employed. This checking becomes especially necessary, if any sort of alteration has been made in any of the arrangements of the furnace.

The following table is that adopted at the French Mint, for the different alloys of silver and copper :---

True Standard.	Standard by Cupellation.	Loss, or quantities to be added to the weights found by Cupellation.
1000	998.97	1.03
950	947.50	2.50
900	896·00	4.00
850	845.85	4.12
800	795.70	4.30
750	745.48	4.52
700	695.25	4.75
650	645.29	4.71
600	595.32	4.68
550	545.32	4.68
500	495.32	4.68
400	396.05	3.95
300	297.40	2.60
200	197.47	2.53
100	99.12	0.88

When other metals besides lead and silver are present in an alloy, the cupel usually affords indications from which it is easy to judge of their nature, and roughly of the amount in which they exist. Pure lead stains the cupel a straw-yellow colour, sometimes verging on orange. Copper gives a grey or dark-brown tint according to its quantity. Iron produces a black stain which is chiefly formed shortly after the commencement of the operation, and gives rise to a dark ring around the sides of the cupel. Zinc leaves a yellowish stain on the cupel, and produces during the process of cupellation a luminous white flame, and abundant fumes of the same colour, which carry off with them a considerable amount of silver. Tin produces a grey slag, and antimony leaves a spongy yellow scoria, which causes the circumference of the cupel to effloresce and split off. The two last-named metals render the cupellation of the alloys in which they exist extremely difficult, and necessitate the employment of a large quantity of pure lead in order to carry off the insoluble oxides formed. When assays of alloys containing silver are frequently to be made by cupellation, it will be found extremely convenient to keep in the laboratory a supply of poor lead, cast in the form of bullets: by this means, the standard of the lead being previously known, it becomes easy, by merely counting the number of pieces added, to know exactly what deduction is to be made for the silver in the poor lead at the termination of the cupellation. When assays containing copper and other metals are to be cupelled, the cupel should be first about half filled with poor lead, and when this has fused and become uncovered, the alloy to be examined is carefully added, enveloped either in paper or in a known weight of thin sheet lead, of which the standard has been previously determined.

Assay of Silver Ores.—In the assay of ores belonging to this class, the object sought is to obtain the metals which they contain in the form of alloys with lead, and these are afterwards passed to the muffle and cupelled in the ordinary way. The method of assaying lead ores containing silver was described when treating of that metal.

Argentiferous minerals containing copper may be assayed as if that metal alone were present, as the resulting button of alloy admits of being readily cupelled with a proper addition of metallic lead. In roasting these ores it is generally necessary to employ a very low temperature only, as, from their great fusibility, they would otherwise be liable to agglutinate, by which the further expulsion of the sulphur would be rendered extremely difficult. It is also of the greatest importance that the whole of the sulphur contained in the ore should be expelled, as otherwise a large portion of the silver present is retained in the slag by the alkaline sulphide formed by the mutual decomposition of the metallic sulphides and the flux employed in the assay.

Ores of silver in which the metals exist in the form of reducible oxides are commonly fused with a mixture of litharge and finelypowdered charcoal, by which an alloy with lead is obtained, which is subsequently subjected to cupellation. The proportion of litharge employed for this purpose must be varied according to circumstances, as the resulting button of alloy should not be too rich, since in that case a portion of the silver is lost in the slag; nor too poor, as the cupellation would then occupy a long time, and a loss through sublimation be entailed. In ordinary cases, if 400 grains of ore be the quantity operated on, a button of 200 grains will be a very convenient amount for cupellation; and this may be obtained by the addition of 300 grains of litharge, and from 7 to 8 grains of finely-powdered charcoal. The whole is to be well mixed with 200 grains of carbonate of soda on a sheet of highlyglazed paper, and afterwards introduced into an earthen crucible, of which it should not fill more than two-thirds the capacity. This is now covered with a thin layer of borax, and fused in an ordinary assay furnace, care being taken to withdraw it from the fire as soon as a liquid and perfectly homogeneous slag has been obtained, as the unreduced litharge would otherwise be liable to cut through the pot and spoil the experiment. When it has sufficiently cooled, the crucible is broken, and the button of alloy obtained is passed to the cupel. In this and all similar experiments it is of course necessary to ascertain by previous experiment the standard of the lead obtained by the reduction of the litharge, in order to be possessed of data from which to make the requisite deduction from the result obtained. With poor litharge, however, the resulting lead contains so small an amount of silver, that, for many commercial purposes, its presence may be entirely neglected.

When other minerals than oxides or carbonate are to be examined, the addition of charcoal, or any similar reducing agent, becomes in many instances unnecessary, as litharge readily attacks all the sulphides, arsenio-sulphides, &c., and oxidises nearly the whole of their constituents, with the exception of silver, whilst a proportionate quantity of metallic lead is at the same time set free. The slags formed in this way contain the whole of the excess of litharge added, and the button of alloy produced is subjected to cupellation in the usual manner. The proportion of oxide of lead added to ores of this description varies in accordance with the amount of oxidisible substances present; but it should in all cases be added in excess, since, if the slags retain traces of any undecomposed sulphide, the whole of the silver contained in the mineral will not be collected in the button of alloy obtained. For the assay of iron pyrites about 30 parts of oxide of lead are required; whilst for mispickel, blende, copper pyrites, grey cobalt, and sulphide of antimony, from 15 to 25 times their weight only may be employed.

The only objection to be made to this method of assay is the large amounts of lead which are produced for cupellation; as pure iron pyrites affords  $8\frac{1}{2}$  parts of this metal, whilst sulphide of antimony and grey copper ore yield from 6 to 7 parts. This inconvenience may, however, be obviated by effecting the partial oxidation of the mineral either by roasting or by the aid of nitre; by the skilful use of which a metallic button of almost any required weight may be obtained.

When this reagent is employed in excess, it determines the

oxidation of all the metallic and combustible substances contained in the mineral, not excepting the silver itself.

But when the mixture contains at the same time a large excess of litharge, and the nitre has not been added in sufficient quantity to decompose the whole of the sulphides present, a reaction is established between the portion of undecomposed sulphide and the oxide of lead added. This gives rise to the formation of a button of metallic lead, which, combining with the liberated silver, affords a button of alloy well suited for the purpose of cupellation. The exact amount of nitre to be employed for this purpose will necessarily depend on the nature and richness of the ores operated on; but it should be borne in mind that  $2\frac{1}{2}$  parts of nitrate of potash are sufficient to completely oxidise pure iron pyrites, and that  $1\frac{1}{2}$  and 2-3rds the weight are in the case of sulphide of antimony and galena sufficient to produce the same effect respectively on those ores.

Assay of Alloys of Silver and Copper by the Humid Way. $\rightarrow$ On account of the difficulty experienced in obtaining perfectly accurate results by the ordinary method of cupellation, a commission was in 1829 appointed by the French Government for the purpose of examining the different processes then employed in the Parisian Mint for the assay of alloys containing gold and silver, and reporting on any modifications which might be thought advantageous.

Gay-Lussac, who was one of the commissioners to whom this question was subjected, proposed the adoption of the liquid method of assay now employed, and published in the name of the commission the details of the various necessary operations. To this report, and Regnault's more recent description of the methods and apparatus at present employed in the French Mint, I am chiefly indebted for the following details.

This process consists in determining the standard of the alloy examined by means of a solution of chloride of sodium, of which the strength has before-hand been accurately ascertained.

The solution of salt employed is so regulated that a decilitre is capable of exactly precipitating 1 gramme of pure silver. To determine the composition of an alloy, 1 grm. of the mixture is dissolved in 5 or 6 grms. of nitric acid, and to this is carefully added the standard solution of common salt from an accurately graduated burette until the introduction of a fresh quantity ceases to be accompanied by a deposit of insoluble chloride of silver. Towards the end of the experiment, when the point of saturation is nearly arrived at, care must be taken to well shake the bottle after the addition of each successive drop of the saline solution, as by this means the liquor is rendered clear through the precipitation of the chloride of silver formed. When the whole of the silver has been thus thrown down, the number of divisions of the burette which have been employed in its precipitation are read off; and, from the amount of chloride of sodium used, the percentage of silver present is at once ascertained.

When an accurate assay has to be made of an alloy of which the composition is before-hand approximatively known, as in the case of a silver coin or a piece of plate, this process admits of being considerably simplified, and at the same time affords results of the most exact description. For this purpose two distinct solutions of common salt are employed: the first, which is known by the name of the *normal solution*, is of such a strength that one decilitre will precipitate 1 grm. of pure silver; the second, called the *decimal solution*, is ten times weaker than the first, and consequently contains in a litre of liquor the amount of chloride necessary to effect the precipitation of 1 grm. of pure silver.

The better to understand this process, let us suppose that a piece of silver money of the French coinage is to be examined, and which, in order to be of the standard quality as prescribed by law, should contain  $1^{607}_{007}$ ths of pure silver. We will assume, then, that the alloy in question only contains  $1^{60}_{007}$ ths of silver, and consequently that 1.116 grm. of the mixture will correspond to 1 grm. of pure silver. This quantity is then cut off the coin, and, after being accurately weighed, is placed in a bottle capable of being perfectly closed by a glass stopper, where it is dissolved in from 5 to 6 grms. of pure nitric acid; and, as soon as the solution has been completely effected, exactly 1 decilitre of the normal solution of common salt is introduced.

It is evident that if, as was first supposed, the alloy has really the standard of  $\frac{4}{1000}$ , the whole of the silver will be precipitated by the quantity of solution added, and that the supernatant liquor will contain no traces of chloride of sodium in excess. If, on the contrary, the standard is higher than that originally assumed, there will still remain a portion of silver in solution; whilst, if it be less, the whole of the silver will have been completely precipitated, but the liquor will contain an excess of chloride of sodium. To ascertain which of these effects has been produced, the bottle is now carefully closed with its glass stopper and briskly shaken until the precipitated chloride has subsided, and the solution become clear.

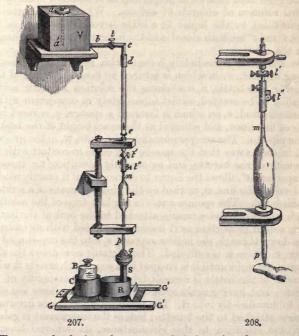
When this point has been attained, a cubic centimetre of the decimal solution of common salt capable of precipitating 0.001 grm. of pure silver is introduced. If any unprecipitated silver remains in the solution, the liquor now becomes cloudy, and after

being again shaken, another centimetre of the decimal solution is added. If, on the addition of this second centimetre of the solution, the liquor again becomes turbid, it is, after being well shaken, allowed to clear, and a third centimetre of the decimal solution poured in, and so on until no further turbidity is produced on the addition of a fresh quantity of the decimal solution. If we suppose that five of the cubic centimetres of the decimal solution. successively added, have produced a precipitate in the liquor, whilst the addition of the sixth has in no way affected its transparency, we may conclude that after the precipitation of 1 grm. of pure silver by the decilitre of normal solution, the liquor still contained at least 4 thousandths of a gramme of silver. From the circumstance of the fifth cubic centimetre of decimal solution having caused a turbidity, whilst the sixth produced no kind of effect on the solution, it is also evident that the liquor at most did not contain more than 5 thousandths of a gramme of silver; and therefore, in adding  $4\frac{1}{2}$  thousandths, we are certain of arriving at the exact result to within, at most, one half-thousandth of the The standard of the alloy examined will therefore be 896 truth.  $+4\frac{1}{2} = 900\frac{1}{2}$  thousandths. When, on the contrary, the cubic centimetre of the decimal solution gives no further precipitate in the solution of silver which has already received the decilitre of the normal liquid, it is evident that the standard of the alloy must be inferior to  $\frac{1000}{1000}$  ths, and consequently the mixture is below the legal title. If in this case its exact composition is required, recourse must be had to a standard solution of silver in nitric acid, so adjusted that one litre of the liquor may contain exactly 1 gramme of pure silver. This is only employed when the alloy to be examined proves to be poorer in silver than was imagined at the commencement of the operation, and is called the decimal solution of silver.

To use this preparation, a cubic centimetre of the decimal silver solution is dropped from a pipette into the bottle containing the assay, and precipitates an amount of salt exactly corresponding to the same volume of the decimal solution of common salt, which was added for the purpose of ascertaining whether the whole of the silver had been precipitated. The liquor is now brightened by agitation, and another cubic centimetre of the silver solution added. If a turbidity is produced, the bottle is again shaken, and a third measure of the solution introduced after the chloride formed has been completely deposited. This is continued until the addition of the silver solution ceases to cause a precipitate in the solution to be assayed. If we in this case suppose that the first five cubic centimetres of the silver solution gave rise to the formation of a precipitate, and that on the introduction of the sixth the liquor remained perfectly clear, it is probable that the fifth cubic centimetre was not entirely decomposed, and it is therefore customary to admit that  $4\frac{1}{2}$  cubic centimetres of the silver solution have been sufficient to effect the decomposition of the excess of chloride of sodium remaining in the fluid after the introduction of the decilitre of the normal solution.

It is consequently evident in this case, that it will be necessary to subtract  $4\frac{1}{2}$  thousandths from the presumed title of the compound, and that the correct standard of the alloy will be expressed by  $896-4\frac{1}{2}=891\frac{1}{2}$  thousandths.

In large establishments, such as the different Mints where great numbers of assays of alloys composed of copper and silver are daily made, the apparatus is so arranged as materially to facilitate the performance of the various operations above described. In the French Mint, where this method of assaying was first employed, the apparatus figs. 207 and 208 has been adopted.



The normal solution of common salt is kept in a large vessel, v, made either of stoneware or sheet copper, and carefully tinned on

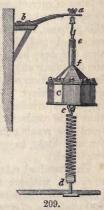
the inside. This reservoir, for the purpose of preventing evaporation, is completely covered by an immoveable lid, provided with a tube,  $a \dot{a}$ , by which the air enters the chamber to supply the place of any portion of the solution that may be drawn off. This vessel, which is supported on a shelf fixed near the roof of the laboratory, is provided with a tube, b c d, bent at right angles at c, and which admits of being closed by a stop-cock, t. The pipette, P, which contains exactly a decilitre of the liquid, is connected with the tube, cd, by means of the tube, de, which contains a thermometer accurately graduated. The metallic connector by which the tube, d e, is fastened to the pipette, P, is provided with two stop-cocks, t' and t'', of which the uses will be presently explained. In conducting an assay, the operator closes the extremity of the pipette with the fore-finger of the left hand, fig. 208, and with the right opens the taps t' and t'', by the first of which the solution enters the burette, whilst from the second the air contained in the glass bulb escapes in proportion as it becomes filled by the normal solution of chloride of sodium. When the burette has become filled by the liquor to a little beyond the mark, m, the cocks, t' and t" are both closed, and the instrument remains charged with the solution.

On the table immediately beneath this apparatus is placed a sliding support, w, in which is secured by means of a ring of thin copper, c, the bottle, B, containing the solution in nitric acid of the alloy to be assayed, whilst immediately in connection with it is a small stand, s, on which is fastened a sponge, q, covered by a piece of fine linen, and situated at the exact height of the beak, p, of the pipette. The assayer now slides the plate, w, in the grooves, G G', in such a way that the sponge may come in contact with the extremity of the burette, and by carefully admitting air through the aperture, t", allows the liquor to descend until it exactly reaches the level of the line, m, marked on the glass by means of a scratching diamond. The sponge removes the last drop of the solution, which would otherwise remain attached to the beak of the instrument, and in proportion as it becomes saturated with moisture it leaks down through the hollow support, s, into the cup-shaped receiver, R, where it is collected. The operator now draws the slide towards the right until it is stopped by a peg, which arrests it when the neck of the bottle is immediately under the extremity of the burette; and, having again opened the cock, t'', he allows the solution to flow directly into it. The last drop of the liquor invariably remains attached to the burette; but, as the instrument is gauged with due attention to this circumstance, its removal becomes unnecessary, and would in fact vitiate the result obtained. As in most instances several assays are being made at the same time,

the weighed quantities of alloy are commonly dissolved in numbered bottles, which are arranged in a metallic frame somewhat similar to a cruet stand, and which, after the introduction of the acid, are placed in a vessel of hot water for the purpose of facilitating their solution.

When the various alloys have become completely dissolved, the nitrous fumes are removed from the bottles by slightly blowing into them through a glass tube, and a decilitre of the normal solution is then introduced into each by the method already described. The bottles are subsequently placed in a second metallic case, c, fig. 209, which, besides being provided with compartments for each phial, is suspended from the extremity of a steel spring, a b, and is steadied from below by the elastic spiral, c d. The bottles, after being carefully closed by their stoppers and fastened in their several compartments, are now well shaken by an assistant, who takes hold of the handle, e f, and briskly agitates the whole apparatus during several minutes. As soon as

the liquors have in this way been rendered sufficiently clear, the bottles are removed from the frame, c, to a black table fitted up with divisions numbered to correspond with those on the phials themselves, care being also taken that each assay be placed in the compartment to which it belongs. The decimal solution which is contained in a phial having a pipette passing through its stopper, is now employed for the purpose of determining the exact standard of the various assays. This pipette is so marked by a line drawn on its surface as to allow the operator to exactly measure out one cubic centimetre of the liquid which it contains. To do this, the point of the forefinger is applied to the upper extremity of



the tube, which, whilst thus closed, is removed from the bottle, and is allowed to drop, by the careful admission of air, until the liquid has fallen to the level of the line marked on its surface. The opening is now closely stopped, and the cubic centimetre of fluid transferred to the first bottle of the series, into which it is permitted to flow on removing the finger from the upper extremity of the pipette.

The same quantity of solution is afterwards successively added to each of the other assays. The assayer now examines each of the bottles in succession, and makes a mark with a piece of chalk on the black table before those in which a precipitate has taken place. These are a second time transferred to the shaking apparatus, in which they are briskly agitated until the liquors have again become clear, when they are taken back to their respective places on the black table, and another cubic centimetre of the decimal solution is added to each in which a precipitate was obtained by the last operation. By degrees the several bottles in which no precipitate has taken place are thus eliminated, and on counting the number of marks placed before them, the number of cubic centimetres of the decimal solution which have been added to each assay is readily ascertained. From this number must be deducted half a centimetre to allow for the loss on the last addition; a portion of which only may be supposed to have suffered decomposition.

The normal solution of chloride of sodium employed in this operation is prepared at 15° C., but as this, in common with all other liquids, expands and contracts in accordance with the temperature to which it is exposed, it becomes necessary to construct a table of corrections to be employed in all cases when the liquor is used at any temperature either above or below this point. For this purpose, the thermometer contained in the tube, d e, must be consulted, and the correction read off from tables prepared for that purpose; but in most instances it is preferred to make use of the following method, by which any error arising from the careless preparation of the normal solution is at the same time fully guarded against. With this view the assayer makes each morning an experiment on 1 grm. of pure silver, at the same time that he is conducting his regular assays of the usual alloys, and from the result obtained by this check he is enabled to correct for any little irregularity in the constitution of the solution employed.

The standard solution of chloride of sodium is made from common salt, without any preliminary purification, and is usually prepared in considerable quantities at a time. For this purpose 500 grammes of common salt are dissolved in four litres of water. The liquor is now filtered, and the amount of water that would be necessary to make a normal solution in, supposing the chloride pure, is added. By this means, a solution roughly approximating only to the composition of the normal liquor is obtained, and of which the exact standard must be ascertained by adding a decilitre to a solution of one gramme of pure silver in nitric acid. The liquor is clarified by agitation, and by the addition of successive centimetres of the decimal solution either of silver or chloride of sodium, the exact amount of free silver or chloride, as the case may be, remaining after the addition of the decilitre of normal solution, is accurately ascertained. When this is known it becomes easy to calculate the quantity of water or chloride which must be added in order to arrive at the correct standard; and when this has been added, other experiments of a similar description are made until satisfactory results are at length obtained. The decimal chloride solution is readily prepared by pouring a cubic decilitre of the normal solution into a bottle of the exact capacity of a litre, and afterwards filling it up with pure distilled water.

To prepare the decimal solution of silver, one grain of pure silver is dissolved in nitric acid, to which distilled water is afterwards added until an exact litre of the liquid is obtained.

When the alloy operated on contains either mercury or lead, the results obtained by the humid assay are no longer exact, as these metals being precipitated at the same time as the silver, decompose a portion of the normal solution by which the experiment becomes vitiated. The presence of mercury in the alloy examined is readily detected by the difficulty which is then experienced in obtaining a transparent liquor by agitation, and when this is observed the experiment must be discarded as unworthy of credit. The assay of alloys containing mercury may, however, be made by the humid process, if a solution of acetate of soda be added to the nitric acid liquor containing the silver previously to the introduction of the normal solution, as this reagent has the property of preventing the formation of the mercurial chloride.

## METALLURGY OF SILVER.

Argentiferous galenas are first treated for lead, and this metal is subsequently freed from silver by the method described, page 502. When silver is associated with copper ores, these are in like manner treated for the copper they contain. The crude metal produced is, however, subsequently fused with the addition of a large quantity of lead, which is afterwards sweated out by a peculiar process, and subjected to cupellation in the ordinary way. In some instances, instead of fusing the crude copper with metallic lead, the ores are mixed with galena, and directly treated in a reverberatory furnace, by which process a copper matt and argentiferous lead are procured.

In many of the continental establishments, the separation of silver from copper is effected by the amalgamation of the last matts obtained during the metallurgic treatment of the latter metal. The ores of silver which contain so small a proportion of other metals that their extraction would not be attended with remunerative results, are, on the contrary, directly subjected to treatment by metallic mercury.

#### SILVER.

The amalgamation of silver ores may be performed by two distinct processes. The first, which is that employed at Freyberg, in Saxony, has been universally adopted in all European establishments. The second, known by the name of the Mexican process, is exclusively employed for the extraction of the silver obtained from the various mines of the New World, and chiefly differs from the European process by being conducted without the aid of any kind of fuel, which in many of the foreign mining districts is extremely scarce and expensive.

## EUROPEAN PROCESS OF AMALGAMATION.

The amalgamation of silver ores is perhaps more systematically and economically conducted at Halsbrücke, in the vicinity of Freyberg, than in any other European locality. The usual constituents of the ores there treated are sulphur, antimony, arsenic, silver, copper, lead, iron, and zinc, which are more or less mixed with various earthy minerals, besides sometimes containing small quantities of bismuth, gold, nickel, and cobalt. In the selection of these ores, they are so assorted as not to contain above 4 per cent. of lead, or 1 per cent. of copper, as from combining with the mercury added, these metals give to the amalgam a pasty consistency, and thereby render the treatment extremely difficult and expensive.

The different ores selected for amalgamation vary in richness from 15 to 200 ozs. per ton. Formerly the mixtures of these ores were so arranged that the charges of the furnaces should always contain from 75 to 80 ozs. per ton. It is, however, now usual to work the poor and rich ores separately, since it is found that the total loss of silver in the residues is thereby considerably diminished.

The mixtures of the poorer ores afford, on an average, from 30 to 40 ozs. per ton; whilst the amount of silver in those of the richer ores varies from 90 to 130 ozs. per ton. It is essential that both mixtures should contain a certain proportion of sulphide of iron, for the formation of the sulphate of iron, which is necessary to the success of the roasting process. The quantity of sulphide of iron present should not be less than about 25 per cent. If the amount of iron pyrites, naturally occurring in the ores, is not equal to this proportion, addition is made either of that mineral or of ready formed sulphate of iron. Frequently, however, the ores at Freyberg contain much more pyrites than is required, and in such cases it is advantageous to subject a few of the most sulphurous to a previous roasting without salt, in order to reduce the average amount in the whole to the right proportion. The ore when prepared is laid on a large floor, 40 feet in length and 12 in width, and on the top of it is thrown about 10 per cent. of common salt, which is let drop from an upper room, through spouts placed in the floor for that purpose. The heap, when it has been thus made up of alternate strata of ore and common salt, is well mixed by being carefully turned over with a shovel, and then passed through a coarse sieve. It is subsequently divided into small parcels, called *roast-posts*, each weighing from  $4\frac{1}{2}$  to 5 cwts. The salt annually employed for this purpose at the Halsbrücke works amounts to 500 tons, and is supplied by the Prussian salt mines.

The mixture of ore and salt is now roasted in reverberatory furnaces, provided with fume flues, for the reception of the pulverulent matters, mechanically taken over by the draught.

The prepared charge is spread on the bottom of the hearth, where it is at first gently heated, for the purpose of expelling the moisture, which to a greater or less extent it invariably contains. During the process of drying, which usually occupies from 20 to 30 minutes, the charge is kept constantly stirred by a long iron rake. The lumps, which are formed in this operation, are then broken down by means of an iron beater (klopfhammer), provided with a long iron handle. The heat is afterwards raised, white fumes are given off, and, in about 2 hours from the commencement, the whole mass has become red-hot. The charge is occasionally turned so that every particle of ore may be equally exposed to the fire; and, during the whole time, the mass must be diligently stirred with the rake. The fire is now left to burn down, and the combustion of the sulphur aided by constant stirring. This must go on without intermission until the mass has become quite dark, and a sample taken from the furnace no longer evolves any odour of sulphurous acid. During this period, the ore increases in volume, and the particles hang so loosely together, that the movement of the cake is scarcely at all impeded. The heat is again raised for about three-quarters of an hour ; the sulphate of iron, formed in the combustion of the pyrites, reacts on the common salt, and causes the evolution of chlorine and hydrochloric acid gases, which, coming in contact with the sulphide of silver, quickly convert it into chloride. The chlorides of the other metals present are at the same time formed, together with sulphate of soda. When the roasting is terminated, the charge is raked from the furnace into an iron barrow, and thence removed to an adjoining floor. The ore is afterwards raised to an upper story for the purpose of being passed through a set of sieves, by which the finer powder is separated from the agglutinated lumps. These are broken down to a proper size, and a part re-roasted by

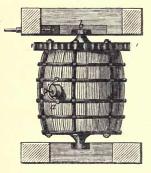
#### SILVER.

adding a small quantity to each of the ordinary charges. The remainder is mixed with 2 or 3 per cent. of salt, and calcined in the usual way. The finer particles, which pass through the sieves, are, on the contrary, taken to a pair of heavy millstones where they are reduced to the state of an impalpable powder.

After the roasting, the ore, besides various earthy salts, consists chiefly of oxide of iron, basic, sulphate of iron, the protochloride, and perchlorides of iron and copper, and portions of oxide and sulphate of copper, sulphate of lead, oxide of antimony, and zinc, and a small quantity of metallic sulphides, in addition to sulphate of soda, and the excess of common salt employed. The compounds of silver, originally present in the mineral, are found to be converted into chloride, with the exception of a trace of metallic silver, and perhaps also of a minute quantity of sulphide and oxide of silver, which remain in the residues. The charge in roasting suffers a considerable diminution in weight, amounting in general to about 10 per cent.

This loss is due to the escape of sulphur, chlorine, particles of salt, zinc, antimony, arsenic, and chloride of iron.

The amalgamation of the prepared ores is performed in 20 wooden casks, arranged in 4 rows, and each turning on cast-iron axles, secured to the ends by means of bolts. These barrels,



210.

which are internally 2 feet 8 inches in length, 2 feet 8 inches in diameter at the ends, and 2 feet 10 inches at the middle or bulge, are made of pine wood,  $3\frac{1}{2}$  inches in thickness, and are strengthened by iron hoops and binders, fig. 210. On one of the ends of each tun is placed a toothed wheel, w, figs. 211 and 212, communicating with a shaft which receives its motion directly from a water-wheel.

Above each of the tuns so arranged is placed a wooden case, c, into which is thrown the prepared mineral. To the bottom of this

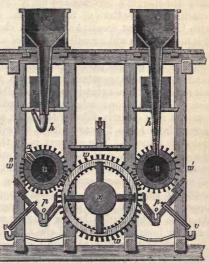
case is fixed a wooden spout, to which is attached a hose made of strong cloth, and terminated by a short cylinder of tin-plate, for the purpose of introducing the powdered ore into the different barrrels, B. Each cask is furnished with a circular opening, a, 5inches in diameter, fitted with a wooden plug, through which has been bored a small hole, provided with a pin made of hard wood for the purpose of running off the argentiferous mercury at the termination of the process. Below the tuns, and a little above the surface of the floor, are placed triangular troughs destined to receive the residual matters at the termination of the operation. At the commencement of the operation 3 cwts. of water

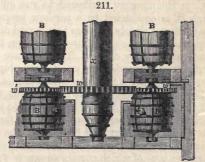
are run into each barrel, after which 10 cwts. of the finely ground and sifted ore are introduced through the hose, b. Each cask should contain from 80 to 100 lbs. of wrought iron, cut into fragments of about an inch square, and 3 of an inch in thickness, and which, in proportion as they become dissolved by the action of the substance with which they are associated, are replaced by fresh pieces.

As soon as the barrels are charged, and the plugs firmly secured in their places by binding screws, the apparatus is thrown into gear by means of a screw and sliding block, fig. 210, and made to rotate with a rapidity of from 12 to 15 revolutions per minute.

At the expiration of 2 hours the machinery is again stopped, for

the purpose of examining the state of the metalliferous paste which they contain. If the charge is too firm, a little water is added, but if, on the contrary, it is found to be too soft, a small quantity of ore is thrown in. When this has been attended to, 5 cwts. of mercury are poured into each cask, and the tuns after being securely closed are again thrown into gear, and kept con-





#### 212.

stantly revolving for about 16 hours, at the uniform rate of 13 turns per minute. During the first 8 hours of this period they are twice examined for the purpose of seeing whether the paste which they contain be of the proper consistence, for if it be too thick the mercury becomes too finely divided, and, if too thin, it remains at the bottom of the cask, and is not sufficiently mixed with the different constituents of the charge. In the first case, it is necessary to add a small quantity of water ; and in the second. a little powdered ore. After the introduction of the mercury the temperature of the casks becomes considerably raised by the chemical changes constantly going on within, so that even in winter it sometimes stands as high as 104° Fahr. At the expiration of 18 hours the amalgamation is ordinarily complete, and the tuns are now entirely filled with water, and again made to turn during from  $1\frac{1}{2}$  to 2 hours with a velocity of only 6 or 8 revolutions per minute. The mercury is by this means separated from the slimy matters with which it was mixed, and collects in one mass at the bottom of the tuns. When this union of the globules of mercury has been accomplished, the different casks are successively thrown out of gear and stopped with the apertures uppermost. The small peg in the bung is now removed, and in its place is inserted a hollow plug, to which is attached a small leathern hose with screw and clasp for choking it when required. The cask is then turned round so that the plug,  $\alpha$ , shall be immediately over the spout, o. The hose being put into the iron tube, p, the mercury is allowed to run off into the gutter, v, by which it is conducted to a receiver prepared for that purpose. The workman closely watches this period of the operation, and the moment any of the earthy matters begin to flow from the orifice it is again tightly closed. The casks are now turned with their apertures, a, upwards, the small hose-plug is removed, and the bung loosened by a few taps with a mallet.

The casks are again turned downwards, the bung is withdrawn, and the muddy residuum discharged into the trough situated immediately under them, from which it flows into large washing vats placed on the ground floor below the barrels.

In 14 days 180 tons of mineral are treated in this establishment, every five tons of which require an expenditure of 15 lbs. of metallic iron, and 2 lbs.  $12\frac{3}{4}$  ounces of mercury, so that every pound of metallic silver produced is obtained at an expense of 0.95 of an ounce of mercury.

During the first 2 hours that the casks are set in motion, and before the introduction of the mercury, the perchlorides contained in the ore are reduced to the state of protochloride, the saline matters are dissolved by the water present, and the particles of chloride of silver thereby exposed. If, instead of this, the mercury were immediately introduced into the casks it would, by reacting on the sesquichloride of iron, &c., become partially converted into calomel, which, not being again reduced during the subsequent stages of the operation, would be productive of a considerable loss of this valuable metal.

This inconvenience is, however, avoided by the action of the metallic iron, as the protochloride thus formed is without action on metallic mercury.

The chloride of silver contained in the roasted ore is decomposed by agitation with the metallic iron and quicksilver, the chlorine of which combines with the iron in the form of protochloride of iron, whilst the silver is dissolved in the fluid mercury. It is probable that this action is galvanic, and if so, the saline solution present is important as a medium for the transmission of the electric currents. The chlorides of lead and copper which may be present are also reduced at the same time as the chloride of silver, and enter into the composition of the amalgam produced.

The slimes conducted to the washing vats before mentioned are mixed with an additional quantity of water, and kept constantly stirred by rods attached to arms of iron and fixed to an upright shaft in the centre of each vat, and turned by a small water-wheel. These vats are furnished with openings at various distances from the bottom, by which the muddy water is successively drawn off into tanks, where the solid matters are allowed to settle. These, if they should contain as much as  $4\frac{1}{2}$  ounces of silver to the ton, are removed to a drying floor, and subsequently re-roasted with 15 or 16 per cent. of iron pyrites, and 5 or 6 per cent. of salt. The calcined residues are afterwards sifted in the usual way, and then, without being ground, are subjected to amalgamation in the barrels for a somewhat shorter period than is customary in the case of ordinary ores.

The quicksilver collected in the bottom of the washing vats is drawn off every five or six weeks, and, from the large proportion of impurities it contains, is treated apart from the ordinary amalgam obtained by tapping directly from the barrels. The mercury and amalgam removed from the casks are afterwards filtered through close canvas bags, by which the liquid quicksilver is separated from the pasty amalgam, which is retained by the closeness of the web, whilst the mercury passes through into reservoirs prepared for that purpose. The amalgam which is retained in the bags consists of a mixture of six parts of mercury and one part of an alloy, composed of about 80 per cent. of silver, and 20 of a mixture of copper, antimony, zinc, lead, and some other metals. The amalgam is subsequently heated in iron retorts placed in suitable furnaces, and the mercury separated by distillation from the non-volatile constituents which are obtained in the solid form. The employment of retorts has almost entirely superseded the iron bells formerly used at Freyberg for this purpose. It is, however, necessary that the condensing tube of the retort be somewhat large, and of such length that the vapours of mercury may be liquefied without the aid of water, otherwise explosions will be liable to take place. Three retorts are at present employed, and into each is placed 450 lbs. of amalgam on iron dishes, which yield about 70 lbs. of *teller* silver. The time required to complete the distillation is generally about 10 hours. The silver thus obtained is usually alloyed with about 20 per cent. of various other metals which, with the exception of a certain proportion of copper, are removed by a process of refining in a large iron crucible, and conducted in the following way:—

The crucible being placed in the furnace and made red-hot, the lumps of silver alloy are successively introduced and brought to a state of fusion. Powdered charcoal is then thrown on the fused metal, and the crucible covered temporarily with a thin plate of iron. This, after the lapse of a few minutes, is again removed, and the impurities which have risen to the surface are, together with the unconsumed charcoal, skimmed off by means of a perforated More charcoal is placed on the fluid metal, and the scum ladle. subsequently removed as before. These operations are repeated, with occasional stirring of the metallic bath, until the metal has become perfectly cleaned. The process generally occupies from 6 to 8 hours, and when completed the metal should be malleable and dissolve completely in nitric acid, to which solution the addition of an excess of ammonia should impart a clear blue colour only. The silver is now cast into ingots of a hemispherical shape, and in this state is sent to the Saxon mint. The dust obtained from the fume flues is from time to time removed, and, after having been sifted, is mixed with and treated as ordinary ore. The slags, sweepings, &c. &c., from the melting operations are crushed and afterwards fused with carbonate of potash and nitre, by which means the silver which they contain is obtained in the form of a metallic button. The supernatant liquor run off from the tanks in which the schlich is allowed to settle, chiefly consists of solution of sulphate of soda and common salt, together with small quantities of sulphate of iron and various other soluble salts.

Amalgamation of Copper Matts at Mansfeld. —In the copper works of Mansfeld, the silver is extracted from the last matts by a process of amalgamation in many respects extremely similar to that employed at Freyberg for the direct treatment of argentiferous ores. The matt operated on is first stamped and sifted, and after-

# EUROPEAN PROCESS OF AMALGAMATION.

wards reduced between two granite millstones to the state of a powder. This fine powder, after being slightly wetted with water. is roasted in a reverberatory furnace, with two soles placed one above the other, and provided with condensation chambers, for the purpose of retaining the fumes and finely divided ore which may be carried over mechanically by the draught. The matt to be roasted is first heated very gently on the upper hearth of the furnace, whilst the calcination of a preceding charge is being completed on the lower sole, which, from being the nearest to the fire, is the most strongly heated. Each charge of powdered matt usually weighs 4 cwts., and is evenly spread over the surface of the floor. and kept constantly agitated by an iron rake, with a view of exposing fresh surfaces to the oxidising influence of the air. At the expiration of 3 hours this roasting is sufficiently advanced, and the ore is then raked out through a door in the side of the furnace, into a bin, where it is allowed to cool. The ore thus prepared is now mixed with 10 per cent. of common salt, and the same weight of very finely-powdered carbonate of lime. To this mixture water is added, and the whole worked into a paste, which is subsequently dried in properly arranged stoves. The dried mass is then ground in a mill to the state of an impalpable powder, and subjected to a second roasting at a much higher temperature than the first, on the lower hearth of the furnace. The carbonate of lime added in this case is for the purpose of effecting the decomposition of the sulphates of iron and copper, which would otherwise be produced in such large quantities as to give rise to considerable loss of mercury in the subsequent amalgamation. In order to ascertain if the roasting is sufficiently advanced, the workman withdraws, from time to time, a small sample from the furnace, and intimately mixes it, in a wooden bowl, with water, and a certain proportion of mercury. This pasty mixture is subsequently washed in a larger quantity of water, by which the lighter earthy particles are removed, whilst the heavier amalgam is collected at the bottom, and from the aspect of this he is enabled to judge whether the operation be progressing favourably or not. When the appearances thus observed are not satisfactory, addition is made either of salt, lime, or roasted matt, in the proportions which may be judged necessary.

This second roasting occupies from one and a half to two hours, at the expiration of which time the charge is withdrawn from the furnace, and amalgamated in casks similar to those employed for the same purpose at Freyberg. Each barrel is charged with 5 cwts. of roasted ore, 75 gallons of warm water, and 80 lbs. of small scrap iron. The tubs are now made to turn for a sufficient time to effect the decomposition of the perchlorides, and 3 cwts. of mercury are introduced. The apparatus is now kept in motion during 14 hours, at the expiration of which time the barrels are filled with water, and kept slowly turning for about two hours, to determine the separation of the liquid amalgam from the earthy matters with which it is mixed. The tubs are afterwards emptied by the same process as that employed at Freyberg, and the copper schlich obtained is afterwards mixed with 15 per cent. of plastic clay, and moulded into cakes, which, after being dried at a gentle heat, are treated in a small blast furnace for the copper they contain.

The silver remaining in the distillatory apparatus after the expulsion of the mercury, is, in these methods, fused in large black lead crucibles, which are filled with the metal to within two inches of the brim, and briskly agitated with an iron rod, whilst the silver is in a fused state. The liquid metal soon begins to give off fumes, and throws up a dark-coloured scum, which is skimmed off, and a fresh coating of charcoal thrown on its surface. The crucible is afterwards covered, and again briskly heated; any fresh slag which may have been thrown up is skimmed off, and the operation is repeated as long as any slag continues to be formed. The silver, which is still contaminated by from 15 to 18 per cent. of copper, is now cast into ingots, which are afterwards refined by a process of cupellation.

# MEXICAN METHOD OF AMALGAMATION.

The ores obtained from the mines of Mexico and Chili, which are situated on the western slope of the Cordilleras, chiefly consist of native silver, natural amalgams, antimonial silver, and the compounds of that metal with arsenic, chlorine, bromine, and iodine. In these localities the metal is generally so widely disseminated in the rock, as to be but seldom visible before the ores have been subjected to mechanical preparation. On being brought to the surface, they are first broken into pieces by men and women, who select the richer fragments, and reject those in which there appears to be no metallic particles. The more productive portions, which are divided into three classes, in accordance with their apparent richness, are pounded by stamping mills, morteros, until they are broken down to the state of fine sand. This not being sufficiently divided for the purpose of amalgamation, is afterwards ground with water in crushing mills, arrastras, until it is reduced to the state of an impalpable paste.

These mills consist of a circular bed-stone of hard granite, surrounded by a wooden tub, in the centre of which is supported a vertical shaft, which carries the mullers by which the grinding is effected, and is supported at its upper extremity by a horizontal beam, to which the upper pivot is attached. This vertical axis is traversed by two horizontal arms, by which the mullers are supported; and to the extremity of one of them, which is left longer for that purpose, are attached the two mules by which the machine is set in motion when water power is not to be obtained. This grinding of the ore is generally performed in a large shed or *hacienda*, in which numerous arrastras are at work at the same time.

In place of this apparatus, a mill of very primitive construction is frequently employed for grinding silver ores. The arrangement of this machine is of the most simple description. A situation is chosen where a small stream of water can be procured, and a fall of some eight or ten feet be obtained: here a circular well is constructed of the whole depth of the fall of water, and about six feet in diameter. In its centre is supported a perpendicular wooden shaft, turning at its lower extremity on a bearing let into a large block of stone, and secured at the other end by a circular wooden collar. This shaft, at a short distance above its lower bearing, passes through a rudely-constructed wooden wheel, around the circumference of which are arranged several spoon-shaped floatboards, making altogether a wheel of about four feet in diameter. These are placed in a somewhat oblique direction around the periphery of the wheel, and are set in motion by the stream of water falling with considerable impetus against them. The upright axis passing through the centre of the well is continued about six feet above its surface, and at about half this height is inserted a horizontal arm, which serves as a spindle for a large granite edgerunner, which is made to revolve in an annular trough, formed either of the same material or of extremely hard wood. The stamped ore which is placed in this trough is gradually bruised down by the weight of the heavy stone rolling on its edge continually over it, and is either taken out and sifted in the dry state, or is more frequently ground into an impalpable paste with water. In this case the annular trough in which the stone revolves is provided with a small aperture at a certain distance from its edge, and from this the finer particles of ore are carried off in suspension by a current of water constantly flowing through the apparatus. The fine particles of ore thus carried off are conducted through a series of pits, where they are allowed to settle, and from whence they are subsequently removed for the purpose of amalgamation.

The stamping mills first used for the crushing of the ores are constructed with equal simplicity, and are set in motion by a small under-shot wheel fastened to the extremity of the wooden axis carrying the cams by which the iron pestles are set in motion. Each of these stamp-heads or pestles usually weighs about 2 cwts. and falls into an oblong mortar, somewhat corresponding in shape, although of larger dimensions. After having been thus reduced to the state of an impalpable powder, the ground ore, or *lama*, is carried to the amalgamation-floor, or *patio*, which is a large enclosure surrounded by high walls, and closely paved with large blocks of granite. The mineral is here spread on the ground in the form of large circular patches called *tortas*, varying from 30 to 50 feet in diameter, and seldom exceeding 1 foot in thickness.

At Zacatecas each torta contains 60 tons of mineral, and is surrounded by a rough enclosure of boards, propped in their places with large stones, and secured at the joints by a lute composed of a mixture of clay and horse-dung, to prevent the escape of the In the centre of the heap of ore so arranged is thrown a lama. quantity of saltierra, salt mixed with various earthy impurities. This is added in the proportion of 150 English bushels to each torta, and is intimately mixed with the lama, first by means of wooden shovels, and afterwards by the treading of horses or mules. When the ore and salt have been thus mixed, the heap is allowed to remain for the remainder of the day without any further preparation; but on the following morning, after about one hour's treading by horses, addition is made of from  $\frac{1}{2}$  to 1 per cent. of roasted copper pyrites, called magistral. This substance contains from 8 to 10 per cent. of sulphate of copper, and this appears to be the active principle through which it affects the necessary chemical changes during the subsequent working of the torta. After this addition of magistral, the torta is again trodden by horses, which are driven by a man who holds the long halter by which they are attached, and stands at the centre of the heap and continually urges them forward.

When the magistral and ore have been perfectly incorporated, a quantity of mercury is added by being filtered through a bag made of coarse canvas, which causes it to escape in innumerable small jets over the whole surface of the pile. A second treading of horses now follows, after which the heap is turned by wooden shovels, and its original form again restored. This alternate turning and treading by horses is repeated every other day, until the whole of the mercury added is found by an assay to have been taken up by the silver. When this combination is found to have taken place, a second quantity of quicksilver is added, and the same operations again repeated until this also has been taken up, when a third supply is generally added : after the due incorporation of which, the ore is removed to the washing backs, where the amalgam is separated from the associated earthy matters.

In order to ascertain the state of the operation, and when a sufficient quantity of mercury has been added, the amalgamator from time to time makes an assay by washing a small portion of the mineral from the torta in a wooden bowl until the earthy impurities have been removed, and the amalgam alone remains in the bottom of the vessel. From the appearance of this he is enabled to judge of the progress of the operation, and whether it be necessary to effect the decomposition of a portion of the magistral by the addition of a little lime, or if, on the contrary, there is a deficiency of this substance. If the surface of the amalgam is of a greyish-white colour, and the mass admits of being readily moulded by the pressure of the finger, it is a proof that the process is favourably progressing. When, on the contrary, the mercury is in an extremely divided state, and of a dark colour, with occasional brown spots, it indicates the presence of too large a proportion of magistral, and the torta is said to be too hot. If in this case the operation were allowed to proceed without any alteration, large quantities of mercury would be lost, and it is therefore necessary to immediately add a certain portion of lime, which decomposes a part of the sulphate and chloride of copper contained in the heap. When, on the other hand, the mercury is found to retain its fluidity, it is considered as a proof that the torta is too cold, and an additional quantity of magistral must consequently be added. These assays are frequently repeated for the purpose of regulating the quantities of mercury to be employed. At Zacatecas, where the average richness of the ore varies from 30 . to 35 ozs. of silver to the ton, the first addition of mercury to each torta amounts to 900 lbs.; the second to 300 lbs.; and the third to 420 lbs.: making a total of 1,620 lbs. of mercury for every 60 tons of mineral treated.

The duration of these operations varies very considerably in accordance with the nature and richness of the ores treated, and the more or less skilful management of the process, as in some establishments the whole elaboration of a torta is in summer completed in fifteen days, whilst in others it occupies from six weeks to two months.

In winter the various reactions are found to proceed less rapidly, and a proportionately longer time is therefore necessary to produce the same effects.

The washing-out vat, or *lavadero*, in which the amalgam is separated from the various sterile matters with which it is intermixed, consists of a large vertical pug-tub, sunk into the ground, and in the centre of which is a wooden shaft furnished with several agitators arranged around it at right angles. This is set in motion by four mules, harnessed to a strong horizontal arm placed a little above the level of the ground: the tub is now filled with water, into which is thrown the amalgamated ore, and this being stirred about by the vertical agitator, allows the particles of amalgam to fall to the bottom, whilst the lighter earthy particles are carried off by a small stream of water, which constantly flows into the apparatus over the side of the tub, through a small aperture prepared for that purpose.

The amalgam thus obtained is afterwards placed in a strong leather bag with a canvas bottom, through which the mercury percolates in a finely divided stream, whilst the pasty amalgam remains behind. This is subsequently pressed in order to free it from a further portion of the adhering mercury, and is then moulded into wedge-shaped masses of about 30 lbs. in weight. To expel the last traces of quicksilver these are laid on the bottom of a furnace provided with an iron spout passing from the centre of the sole into a receiver containing water introduced beneath it. Around the upper aperture of this pipe the wedges of amalgam are arranged in the form of a dome, which is afterwards covered by an iron bell, and heated by a charcoal fire in a way very similar to that employed at Freyberg, and in other European establish-The sublimed mercury is condensed in the vessel of ments. water placed beneath the furnace, and on the cooling of the arrangement this is removed, and the crude silver taken away to be fused into bars. By this system of amalgamation every part of silver obtained involves the expenditure of 1.3 parts of mercury, which is lost during the process.

In this process the sulphate of copper of the magistral and the common salt mutually decompose each other, and give rise to the formation of chloride of copper and sulphate of soda. The metallic silver present in its turn decomposes the chloride of copper, and reduces it to the state of subchloride, whilst it is itself transformed into chloride of silver. The subchloride of copper is now dissolved in the solution of chloride of sodium, and reacts on the sulphide of silver with the formation of sulphate of copper and chloride of silver. The chloride of silver thus formed reacts on the metallic mercury, a portion of which is converted into subchloride, whilst the remainder combines with the silver thus liberated. In this case, as well as in the process employed at Freyberg, it is of the utmost importance that no free chloride of copper should be present, as, by giving up to the mercury one half of its chlorine, a considerable loss of that metal is produced. When this occurs, lime is added for the purpose of decomposing the excess of chloride of copper, by which it is rendered neutral, and its prejudicial action on the mercury arrested.

Alloys of Silver .-- On account of its softness, silver is seldom employed in a pure state, but is commonly alloyed with a certain amount of copper, by which its hardness is remarkably increased. In this way considerable quantities of copper may be added without materially diminishing the whiteness of the original metal, since a mixture of seven parts of silver and one of copper still retains a decided white colour, although of a less pure tint than that exhibited by virgin silver. In order to improve the colour of objects formed of alloyed silver, it is usual to subject them to an operation by which their surfaces are rendered almost free from the presence of the metal so combined. For this purpose the article to be whitened is externally oxidised by being heated nearly to redness, and afterwards plunged, whilst still hot, into water acidulated either by nitric or sulphuric acid, by which the oxide of copper formed is immediately removed. The object, after being thus treated, necessarily presents a matted surface from the isolation of the particles of silver ; but this appearance is readily removed by rubbing with a burnisher.

The silver used in the preparation of coin, and for the manufacture of silver plate, consists of an alloy of silver and copper in different proportions, fixed by the legislature of the country in which the mixture is worked. In this country the same alloy is employed both for the purposes of the Mint and the uses of the silversmith: it is composed of a mixture of 111 parts of silver and 9 of copper, and is known by the name of standard silver. To prevent fraud, all silver vessels are required to be stamped by the Goldsmiths' Company, who are empowered by Government to search all silversmiths' shops, and seize all articles which have not been impressed with the Hall mark of the Company. For the assay of the articles, and the impression of the Company's stamp attesting its quality as standard silver, one shilling and sixpence per ounce on the weight of the object is charged. Of this amount the larger proportion is paid over to the Government in the form of a tax, whilst a small sum is retained as a compensation for the trouble incurred in making the assay. In France, three different standards are employed. The alloy used for the silver currency of the country is composed of 9 parts of silver and 1 of copper; for plate, a mixture of 91 parts of silver to 1 a part of copper is employed, whilst for small articles of silver used for ornaments an alloy of 8 parts of silver to 2 of copper is allowed.

Silver solder consists of 667 of silver, 233 of copper, and 100 parts of zinc. Besides being used for the manufacture of various

objects of luxury, silver is also extensively employed for externally plating the surfaces of articles made of less expensive metals. For this purpose it is either applied to the surface of the object in the form of an amalgam with mercury, which latter metal is afterwards expelled by heat, or is deposited in the metallic form from its solution by the agency of a feeble electric current.

# GOLD.

# Equiv. = 98.33. Density = 19.3.

GOLD is possessed of a characteristic yellow colour, and is the most malleable of all the metals. One grain of pure gold may be beaten into a leaf having a superficies of 56 square inches, and which, from this measurement, and the known specific gravity of the metal, is calculated to have a thickness of one two-hundredthousandth of an inch. The wire used by lace makers is drawn from ingots of silver, previously gilded; and on calculating the length and circumference of the wire thus prepared, together with the weight of gold originally employed, its coating of that metal is found to be at least twelve times thinner than ordinary goldleaf; but still, so perfect is the gilding, that a powerful microscope fails to detect the slightest flaw or imperfection on its surface.

When in extremely thin leaves, gold is, to a certain degree, transparent, and, on being held between the observer and the light, appears of a beautiful green colour. When large quantities of gold have been fused, and then slowly allowed to cool, cubes more or less modified on their edges and angles are frequently obtained. Native gold likewise affords numerous well-defined crystals belonging to the cubic system, and of these the greater number are affected by the faces of the regular octahedron, or dodecahedron.

It fuses at a temperature estimated by Daniell at 2016° Fahr., and when still more strongly heated, affords sensible metallic vapours. If the charge of a powerful electric battery be passed through an exceedingly fine gold wire, it becomes entirely dissipated; and when a sheet of white paper is held beneath it at the time of the discharge, it becomes stained with a purple line caused by a deposit of minutely divided metallic gold. If, instead of a sheet of white paper, a plate of polished silver be employed, it is traversed by a brightly gilded line, which is firmly attached to its surface. A globule of gold, when exposed between two charcoal electrodes to the action of a powerful voltaic battery, enters almost immediately into fusion, and gives off abundant metallic fumes, by which its weight is rapidly diminished. When precipitated from its solutions, gold assumes a darkbrown colour, but on being rubbed by a piece of polished steel, or other hard body, readily assumes its ordinary colour and metallic aspect. If precipitated gold in this form be heated to whiteness, and when in that state struck repeatedly with a heavy hammer, its particles readily become welded and united into a solid mass without their having undergone actual fusion.

The gold used in the manufacture of jewellery, as well as that employed for being coined into money, is invariably alloyed by some other metal, such as copper or silver, and is therefore never To obtain a button of pure gold from these absolutely pure. mixtures, a few fragments of old jewellery may be dissolved in aqua regia, and the solution gently evaporated to dryness for the purpose of expelling any excess of acid. The residue is now treated with hot water, by which it is dissolved, with the exception of any chloride of silver which may be present. The chloride of silver is then separated by filtration, and an excess of protosulphate of iron in solution added to the filtrate, which is placed in a warm place, and allowed to stand for several hours. A reaction is thus effected, by which metallic gold is deposited, whilst the chlorine with which it was originally combined unites with a portion of the iron of the protosulphate, which is thereby converted into persulphate, whilst perchloride of iron is at the same time formed. The precipitate thus obtained, after being digested for some time in weak hydrochloric acid, and well washed in distilled water, is mixed with a small quantity of borax and nitre, and finally fused in an earthen crucible strongly heated in an assay furnace. On breaking the pot after it has been allowed to cool, it will, if the experiment has been carefully conducted, be found to contain a button of pure gold. Pure gold may be indefinitely exposed to the action of air and moisture without becoming in the least degree tarnished, nor is it oxidised by being kept in a state of fusion in open vessels. Neither sulphuric, hydrochloric, nor nitric acids attack gold, even when in a finely divided state; but by aqua regia it is readily attacked, and dissolved in the form of chloride. Gold may also be dissolved by hydrochloric acid, to which has been added some substance capable of liberating chlorine with facility: among these may be mentioned chromic acid and peroxide of manganese.

Bromine, even in the cold, rapidly attacks this metal, although by iodine it is but sparingly acted on, even by the aid of heat.

Gold is not directly attacked by sulphur at any temperature; but when fused with the alkaline sulphides, is rapidly acted on with the formation of a double sulphide, in which the sulphide of gold acts the part of an acid. Gold is totally unacted on by the caustic alkalies, as well as by their carbonates and nitrates.

#### SOURCES OF GOLD.

This metal is found exclusively in the native state, but is seldom pure, and commonly contains a certain portion of silver, and not unfrequently copper and iron.

Native gold generally presents the characteristic yellow colour peculiar to this body when in a state of purity, but its natural surfaces frequently require to be rubbed with some hard substance before they assume the ordinary appearance of manufactured gold. The hardness of gold is less than that of iron, copper, or silver, but greater than that of either lead or tin. When broken by repeated bendings, it presents a matted silk-like structure, which is more or less fine in accordance with the purity of the specimen. Native gold occurs crystallised, in branches, in filaments and plates, traversing the fissures of different kinds of rocks, in disseminated grains, and in *pepitas* mixed with, and forming a part of, various alluvial deposits. In the latter form by far the greater portion of this metal is procured; but as these sands are themselves the product of the destruction of auriferous rocks, the metal which they contain must be regarded as the debris resulting from the disintegration of the matrix in which it was originally enclosed. Crystalline specimens are likewise numerous, the cube being in all cases the primitive form. Crystals seldom occur isolated, but are more frequently grouped together in the form of irregular branches. Their faces are generally dull, and in most instances slightly rounded, even in specimens directly extracted from the vein, and which, consequently, cannot have been exposed to attrition.

The small branches of gold which frequently occur in auriferous rocks, when closely examined appear to consist of a series of minute octahedrons, implanted the one on the other, so as to form a sort of chain.

The grains and fragments found in alluvial deposits vary considerably in size, but are generally very small.

When of the size of a pea and upwards, they receive the name of nuggets; and in some localities pieces of the size of a nut are not of unfrequent occurrence.

Among the most remarkable masses of gold which have been found may be cited the following :---

The largest mass found in the United States was discovered in Cabarras County, North Carolina, and weighed 37 lbs. troy. In Paraguay, masses of gold varying from 1 to 50 lbs. in weight

### GOLD.

were some years since obtained at the foot of one of the highest mountains. Various lumps varying from 16 to 17 lbs., and one weighing 27 lbs., have been found in the Ural district; and in the valley Taschku-Targanka a fragment was detached in 1842 which weighed very nearly 100 lbs. This specimen has been deposited in the Museum of Mining Engineers at St. Petersburgh.

Some very large specimens of native gold have likewise been obtained from various parts of California; and masses weighing above a hundred weight have been procured from the Australian diggings.

The composition of various specimens of gold, as obtained from different localities, is given in the following table :---

Experimenters.	Locality.	Gold.	Silver.	Copper.	Iron.
G. Rose	From the auriferous sands of Schabrow- ski	98·76	0.16	0.32	0.02
	From the sands of Petropawlowsk near Bogoslowsk	86·81	13.19	0.30	0.24
	From the mines of Beresof	93.78	5.94	0.08	
	From Alexander An- drejewsk nr. Miask	87.40	12.07	0.09	-
	From the mine of Sinarowski, Altai	60.08	38.38	0.33	
	From the mine of Santa-Rosa	64 <b>·9</b> 3	35.07		Agentives
Boussingault .	{ From Transylvania .	64.52	35.48		
	Gold from Ojas-Anchas	84.50	15.50		
	,, Rio-Sucio	87.94	12.06		
D'Arcet	,, Baja , Senegal .	88·15 86·97	11.85 10.53		
	{ ", Brazil.	94.00	5.85		

In the Gongo Soco mines in Brazil, an alloy of gold and palladium of a pale yellow colour is sometimes found; and in some parts of Columbia a somewhat similar mixture is procured in which the palladium is replaced by rhodium. The greater portion of the gold of commerce is obtained from Asiatic Russia, Brazil, Africa, Transylvania, the East Indies, Australia, and California. The annual supply procured from these several sources is estimated at about 150,000lbs., having a value of above nine millions sterling.

The chief sources of this valuable metal are the deposits of sand and gravel produced by the disintegration of siliceous, granitic, and other igneous and metamorphic rocks, which have been transported by the agency of water from districts in which gold is disseminated. In addition to the supply afforded by the washing of these sands, a certain quantity, amounting to about onetenth of the total annual production, is obtained from minerals, in which it occurs in the form of minute spangles, disseminated in a matrix of quartz found in the form of veins in schistose rocks. In these cases the quartz is generally more or less porous, and almost invariably stained of a brown rusty colour from the presence of peroxide of iron. The working of such veins has, however, seldom been attended with such satisfactory results as have been obtained from alluvial washings,-since the labour of extraction is not only considerably greater, but, from the difference of density existing between the particles of gold and those of disintegrated rock, these sands are continually becoming enriched by the action of water flowing continually over them. In Brazil, the mines of Gongo Soco and some others have been, however, extensively worked on veins; but, from the heavy expenses entailed by this method of exploration, and from the circumstance that the mineral obtained is but little richer than the alluvial sands, these undertakings are seldom extensively conducted.

The gold mines of Russia and Siberia extend first on the eastern flank of the Ural, in a belt extending through five or six degrees of latitude to the north and south of the town of Ekatharineburg. There is likewise a second deposit of a similar nature in the governments of Tomsk and Yeneseik, where low hills extend northward from the great chain of the Altai mountains, and cover a space of many thousand square miles.

The most celebrated mines of the first-named district are those of Berezovsk, which yielded during the century previous to the year 1841 about 24,500 lbs. of gold, which was extracted from something less than a million of tons of auriferous mineral. The matrix usually consists of coarse siliceous sand, but veins containing auriferous quartz are also actively wrought. These veins are worked by vertical shafts, from which galleries are extended in the direction of the run of the lodes: this is, however, the only instance which occurs in the whole Russian territory where subterranean workings are resorted to for the extraction of gold. The annual supply of gold furnished by Russia and her dependencies is estimated at nearly 40,000 lbs. weight, and is valued at two and a half millions sterling.

The mines of Brazil, are mostly situated at the foot of the great mountain chain running parallel to the coast from the fifth to the thirtieth degree of South latitude. It also occurs in greater or less quantities in the beds of the streams forming the upper branches of the Francesco, Tocantins, Araguay, and Guaporé, but more particularly in the first. The rock in these localities consists of primitive granite inclining to gneiss, and the soil, which, from being highly ferruginous, is of a red colour, often extends to a great depth. The gold is chiefly found in a bed of gravel and rounded pebbles, called *cascalho*, immediately in contact with the surface of the solid rock.

Wherever water is found in the valleys, large excavations are made for the purpose of washing these deposits; and by conducting a rivulet to the declivities of many of the hills, gold is frequently collected from a short distance only beneath the roots of the grass.

The most recent washings are established in the vicinity of Villa Rica, near the village of Cocaes, where the gold occurs either mingled with the sands of the rivers, or in the alluvial deposits lying in valleys between elevated hills. Gold is also procured in other parts of the province of Minas Geraes, and is extracted both by subterranean excavations and by the washings of alluvial deposits.

The greatest quantity of gold found in these localities was obtained between the years 1753 and 1763, since which time the annual produce has been continually on the decrease. Between these periods the yearly product amounted to 16,000 lbs., but between the years 1801 and 1820 was reduced to 3,540 lbs. only.

Gold is likewise found in many other parts of South America; but that of Mexico and some other districts is constantly associated with silver. The only auriferous veins worked in that country, as gold mines, are in Oaxaco, where they traverse formations of gneiss and mica-slate.

The gold obtained from Africa is principally found between Darfur and Abyssinia, as also to the south of the great desert from the mouth of the river Senegal to the Cape of Palms: a certain amount is also collected on the Mozambique coast, between latitudes  $22^{\circ}$  and  $25^{\circ}$  South. Gold is likewise obtained from the sands of the Niger, the Gambia, and the Senegal, as well as from the gold coast near the equator, from which large quantities of this metal are annually exported. The total yearly supply from this continent is estimated at 5,000 lbs. avoirdupois, worth about £300,000 sterling.

The gold obtained from Europe, with the exception of European Russia, is too small in quantity to materially affect its commercial value. The most important of these deposits are in Transylvania, although the sands of the Moldau and other Bohemian rivers also contain a certain quantity of this metal. The annual supply from Hungary, according to Villefosse, amounts to 2,810 lbs. weight, worth  $\pounds 176,000$  sterling. The valley of the Rhine, between Basle and Mannheim, is also known to be auriferous; and, according to M. Daubrée, a French engineer, some of the richest zones would admit of being profitably treated.

The Spanish mines, which were anciently rich and actively carried on, are now neglected, as are also those of the Tagus, the Rhone, and the Danube. The British islands also furnish from time to time small quantities of gold, although seldom in sufficient amount to be equivalent to the cost of extraction. The principal localities in which gold has been found in the United Kingdom are in Ireland and Wales, although specimens are occasionally obtained from the Cornish stream-works, and from the district of Lead-hills in Scotland, where, in the time of Elizabeth, extensive washings were carried on for its extraction. Gold likewise occurs at Cumberhead in Lanarkshire, and Glen Turret in Perthshire. The quantities obtained from the above localities, are, however, extremely small; and, notwithstanding that small accumulations and occasional lumps have sometimes been discovered, no workings of a regular kind, and on an extensive scale, have been attempted, excepting in Ireland.

In that country a considerable quantity of native gold was accidentally discovered towards the close of the last century, disseminated in the beds of the streams which flow from the northern flank of Croghan Kinshela, on the confines of Wicklow and Wexford, and in the immediate vicinity of the junction of the granite and clay-slate. This gold was found in massive lumps, one of which weighed nine, another eighteen, and a third twenty-two ounces. Soon after the discovery of this gold, its extraction was undertaken by the Government, under the management of Mr. Weaver, and some other gentlemen. These workings were continued during about two years, and in this time 945 ounces of gold were obtained, which was sold for £3,675, but the cost of production exceeding the return, the Government works were suspended, and have not since been resumed. Before, however, the district was taken possession of by the Government, a quantity of gold of the value of at least £10,000 is said to have been collected by the country-people living in the vicinity of the deposit.

Considerable excitement has recently been created by the reported discovery of auriferous veins in Great Britain, some of which are stated to be of extraordinary richness. From my own observations, as well as from the investigations of many of my friends, who have had ample opportunity of testing the accuracy of the various statements which have been put forth on this subject, I am of opinion that the richness of this country for gold has been decidedly overrated. It is consequently not improbable that, in the course of a short period, we may hear less not only of the auriferous deposits themselves, but also of the different contrivances which have been recommended for the treatment of the ores, and which, in most instances, are totally unfit for the purposes for which they are intended.

In addition to the supply of gold obtained from the plains of Siberia, Asia has also contributed considerable quantities of this metal from the rivers of Syria and other parts of Asia Minor, as well as from the peninsular of Hindostan, and various islands in the Indian Ocean.

The gold mines of the United States of America are chiefly situated along the eastern slope of the Appalachian Chain, from Maine to Alabama, from whence the deposit, although chiefly confined to the States of Virginia, North and South Carolina, and Georgia, extends into Canada. Among the principal gold mines of Virginia, may be mentioned those of Spotsylvania on the Rappahannock, the United States Mines, and those in Stafford County; the Culpepper mines on Rapidan river, in Orange County, in Goochland County, in Louisa County, and Eldridge's mine in Buckingham County. In North Carolina the gold region is chiefly confined to the three ranges of counties between Frederick and Charlotte, running in a line nearly parallel with the coast. The Mecklenburgh mines are principally worked on veins, whilst those of Burke, Lincoln, and Rutherford, are worked on alluvial deposits. The principal gold districts in South Carolina are the Catawba and Lynch's Creek regions, chiefly in Lancaster and in Picken's County, adjoining the State of Georgia. The most remarkable mines in Georgia are those of Shelton in Habersham County, but some recent operations have been also commenced in Cherokee, Hall, and Rabun Counties.

The gold district of California, as far as at present known, occupies the northern part of New California, commencing near the mouth of the Sacramento river, in lat. 39° North, and long.  $122\frac{1}{2}$  West, about 100 miles to the north-east of the bay and town of San Francisco. The alluvial deposits in which the gold is found consists of sand apparently produced by the disintegration of quartoze granite, and porphyroid rocks, but of the geological structure of the country little is yet accurately known. Col. Fremont describes the valley of the Sacramento as taking its origin in several parts of the Sierra Nevada, and in the transverse range proceeding from the coast at Cape Mendocino. Several of these affluents, and particularly that called the Rio de los Americanes, which falls into the main river in the vicinity of San Francisco, have been found particularly productive. At a distance of about twenty-five miles up this stream are situated the Mormon Diggings, or Lower Mines, where successful and very extensive washings have been carried on. Five-and-twenty miles north of the Rio de los Americanes, the stream called Rio de los Plumas falls into the Sacramento, and here also are established diggings at which very large profits have been realised. Besides these localities, the whole of the affluents of the Sacramento have afforded gold wherever they have been explored, and the whole of the country from the Ajuba to the San Joaquin rivers, a distance of 120 miles, and from the base towards the summit of the mountains as far as Snow Hill, have proved to be auriferous.

The first official notification of the discovery of gold in our Australian colonies is contained in a despatch from Governor Fitzroy to Earl Grey, and bears date May 22, 1851. In this it is announced that a gold field had been discovered westward from the town of Bathurst, and at a distance of about 150 miles from Sydney.

The existence of gold among the various mountain chains of New South Wales had not only been predicted by Sir Roderick Murchison as early as the year 1848, but had also been insisted on by Mr. Clarke, a native geologist, who expressed his conviction that the Blue Mountains would at some time prove to be auriferous. These views were to a certain extent confirmed by the circumstance of a shepherd having long been in the habit of bringing into Sydney, for sale, fragments of native gold, but refused to state from whence he had obtained them.

About two years before the actual discovery of gold in the colony, a Mr. Smith, who was engaged in some iron works in the vicinity of Berrima, produced to the Colonial Secretary a lump of gold imbedded in quartz, which he said he had picked up in a place which he offered to make known to the Government on being previously rewarded for the intelligence by the payment of a considerable sum. The reply to this offer was, that no blind, bargain upon such a subject could be entered into, but that if Mr. Smith thought proper to trust to the liberality of the Government he might rely on being rewarded in proportion to the value of the alleged discovery, when that had been ascertained.

To the conditions of this proposal Mr. Smith refused to accede, and here, for a considerable time, the matter rested, as, apart from the suspicion entertained by the governor that the piece of gold produced by Mr. Smith might have come from California, or some other foreign locality, he was of opinion that any investigation instituted by the Government with a view of ascertaining whether gold did in reality exist to any amount in that part of the colony, which, from its geological formation, might be supposed to afford it, would be liable to agitate the public mind to such an extent as to divert the attention of the colonists from their proper and more certain avocations.

On the 3rd of April, 1851, Mr. Hargraves, who had recently returned from California, addressed a letter to the Colonial Secretary, to the effect that, having occupied himself for two months in exploring a considerable extent of country, in which, from his experience in California, he was led to believe gold was to be found, he had prosecuted his speculation to a successful issue, and offered to point out to the Officers of Government the localities in which he had discovered gold, on condition that he should receive the sum of five hundred pounds as a compensation. To this proposal a reply was returned similar to that given on a former occasion to Mr. Smith, and on the 30th of April Mr. Hargraves addressed a second letter to the Colonial Secretary, expressing his willingness to leave the remuneration of his discovery to the liberal consideration of the Government, and naming the localities from which he had obtained specimens of gold.

On the 8th of May the discovery became generally known, as some persons, who had been employed under the directions of Mr. Hargraves at Summer Hill Creek, one of the localities named by him as auriferous, had obtained several ounces of gold; and on May the 13th, very great excitement prevailed from a report that a solid piece of gold, weighing 13 ounces, had been obtained. This, on inquiry, proved to be correct, and hundreds immediately started for the diggings.

The Government now issued a proclamation declaring that all persons digging for gold without a license would be proceeded against; and regulations were issued authorising the Crown Commissioners to grant such licenses for a fee of £1 10s. per month. The Commissioners were also furnished with a force of ten men, for the purpose of collecting these fees, and for the maintenance of order; strong detachments of police being at the same time posted along the principal roads leading to the gold fields. Mr. Hargraves, and the Government geological surveyor, Mr. Stutchbury, with whom Mr. Clarke was afterwards associated, were now ordered to make an immediate survey of the various localities in which it was thought that gold would be found.

As might be expected, the excitement spread rapidly, and large numbers of persons left their employments and flocked to the spot. On the 19th of May 400 persons were reported to be occupied at the diggings on Summer Hill Creek. On the 29th, 1.000, and on the 5th of June 1,500, were stated to be thus employed. About the 14th of June a fresh enterprise was opened on the Turon River, one of the localities first pointed out by Mr. Hargraves, and afterwards more specifically indicated by Mr. Stutchbury. This at once carried off a large number of those previously employed at Summer Hill Creek, or Ophir, as that locality is now called, since early in July it was stated as probable that at this place the number of diggers for the month would not exceed 400, while at Turon it would be considerably above 1,000. In December the number of diggers on the Turon amounted to 6,000; and since that time gold fields have been discovered in various places, of which the following are among the most productive :--- Muckewa Creek, Louisa Creek, and Meroo Creek in the county of Wellington, Frederick's Valley, Campbell's River, and Winburndale Creek in the county of Bathurst, Abercrombie River in the county of Georgiana, and Araluen River, and its various tributaries in the county of St. Vincent's.

A short time after the announcement of the existence of gold in the colony of New South Wales Proper, a still more amazing discovery was made in Victoria. In a despatch dated 25th of August, 1851, Lieutenant-Governor Latrobe communicated to Earl Grey that large auriferous deposits had been found in that colony. The three localities first named were Clune's diggings, about forty miles from Melbourne, where the gold was found in an alluvial deposit, chiefly consisting of quartz gravel; at Boninyong, or Ballarat, situated on the river Leigh, about seventy-five miles from Melbourne, and forty-five from Geelong, where the gold was sometimes imbedded in compact quartz; and at Deep Creek, only nineteen miles from the capital, where the precious metal was found to exist in connection with slate rock. At Ballarat, from whence the greatest quantity of gold was obtained, the metal is found in lumps of various sizes-sometimes in the superficial soil, but more generally scattered through three or four successive strata, principally composed of clay and gravel, and occupying from 10 to 30 feet in depth. The richest deposits are, however, found in certain small beds of blue clay, four or five inches in thickness, and lying almost immediately above a stratum of pipe-clay, in and below which no gold has been found. In addition to the above localities gold was also found near Geelong; at Mount Disappointment; in the Pyrenees; and finally the people of Melbourne began to break up the streets, which were macadamised with quartz pebbles obtained from the gold districts. By this time Melbourne and Geelong were almost emptied of their male inhabitants. shopmen and day-labourers were the first to leave, and the superior class of farmers and tradesmen speedily followed, partly from

sharing the same mania, and partly because, after losing their subordinates, they could do nothing else. In some cases they placed themselves at the head of digging parties, consisting of their dependents; and in others worked singly and with their own hands. At this time the public excitement became so great that it was found impossible to retain the services of the government *employés* without an addition to their salaries of first 25, and subsequently 50 per cent. In about a month after this a fresh gold field was discovered in the range of Mount Alexander, on the east of the Lodden River, and about seventy miles north-west of Melbourne, which shortly surpassed in richness not only the Ballarat diggings, but all others which had been previously discovered.

The whole structure of Australian society now became completely disorganised. The number of diggers at Ballarat, which had previously risen to 6,000, were quickly reduced to about 1,600, whilst the number at Mount Alexander soon amounted to 20,000. From this time gold began to be collected from all the various streams flowing from the Mount Alexander range, on the Goulburn River, and throughout the whole of the Omee country, by which the supply was so far increased that gold soon arrived at the seaports at the rate of two tons per week. At the present moment a vast number of other localities have been discovered, and up to the receipt of the latest intelligence the supply of the precious metal appeared to be on the increase.

# MECHANICAL AND METALLURGIC TREATMENT OF GOLD.

From the great difference of density existing between the particles of gold, and the siliceous and ferruginous gravel with which it is associated, its separation from these bodies becomes an extremely simple operation. The methods practically employed for the purpose of effecting this object, vary both with the localities in which the operation is carried on, and also in accordance with the nature and composition of the mineral operated on. In many localities where hand-washing is practised, the instrument em-



ployed is a small iron or zinc pan, fig. 213, from which the lighter and stony matters are carried off by suspension in water: the residuum thus obtained contains the greater part of the gold, which is subse-

quently separated by amalgamation. In Hungary, in place of the pans above described, the washing is conducted on inclined tables, traversed by a number of transverse grooves. The inclination of these tables is varied in accordance with the nature of the mineral treated, and the sand to be washed is placed in the first groove of the series, and then exposed to a current of water until the gold, together with a small portion of the sand, has collected towards the lowest furrow. The matrix is now removed into flat wooden basins, where the whole of the stony impurities are separated by a careful washing.

In Brazil, the method of proceeding anciently employed was to open a square pit in the soil until the cascalho or auriferous stratum was attained, when this was broken up with pickaxes and placed in a wooden vessel, narrower at the bottom than at the top. These cases were exposed to a stream of running water, and briskly shaken from side to side until the whole of the earth was washed away, and the metallic particles alone remained. All these workings were situated either in the dried up beds of rivers, or in the table lands over which a stream of water had at some former period flowed. At the present time, instead of opening the ground by manual labour, and afterwards carrying the auriferous gravel to a stream for the purpose of being washed, the water is conducted directly to the mining ground, and by thus washing away the mould, and exposing without the trouble of transporting the cascalho to the action of a stream of water, a great economy of labour is effected.

River mining, from the simplicity of the operations required, is the most easily and readily performed, and consequently by far the greater proportion of the streams which are known to be auriferous, are wrought in some part of their courses. The auriferous veins which traverse some of the mountain districts, although occasionally affording much larger quantities of the precious metal, require the expenditure of a greater amount of both labour and capital, and, therefore, much fewer mines of this description are undertaken. When worked, however, these veins are not often laid bare by subterranean excavations, but are explored by open cuttings made by clearing away the soil directly from the surface. The washings of this kind in the vicinity of St. John del Rey were formerly very rich, but have recently diminished considerably in importance. The principal digging in this locality is now situated on the eastern side of the hill, in immediate proximity to the town, and consists of an open area, of which three sides have been excavated in the solid rock, whilst the fourth, which fronts the west, is left open. The rock here consists of a soft sandstone, or indurated clay, mixed with mica, and is wrought by the aid of numerous streams of water divided into small rivulets, and conducted down its sloping sides. In working the mine the

loosened soil is thrown into these channels, and kept in suspension by constant agitation, until it reaches a well sunk at the bottom of the excavation, and where the heavier and auriferous particles are carried by the current. This pit is occasionally emptied, and its contents again subjected to a second series of washings, by which the particles of gold are finally obtained in a pure state. By this way of mining, large masses of gold or *caldeiraos* are occasionally met with, but in most instances the chief supply is derived from the smaller particles obtained by the repeated washings of the sands collected in reservoirs situated at the bottom of the excavations.

In the district of Lower Parahybuna, large quantities of auriferous sand are annually dredged from the bottom of the river by means of windlasses and iron scoops. The sands thus obtained are transported in canoes cut out of a solid log of wood, and externally formed like a butcher's tray, whilst they internally represent a three-sided prism, of which one of the acute edges forms the line of the bottom. To each of these canoes is allotted a gang of four blacks, three of whom superintend the boat and dredge, whilst the fourth is on the platform ready to receive the sand brought up by the iron scoop. Each of these boats will sometimes collect three quarters of an ounce of gold in the course of a day, but the quantity obtained is extremely small in proportion to the amount of sand which has to be washed. In the neighbourhood of Villa Rica, once remarkable for its richness in this metal, but at present comparatively impoverished, various methods of extraction are adopted; not only the auriferous sands are subjected to careful washing, but numerous drifts and levels have been extended into the softer parts of the mountain. Both these excavations and the river washing are entirely conducted by negroes, of whom numbers are always to be seen thus employed in the Oiro Preto and Do Carmo. These gold-washers are each dressed in a leathern jacket, and are furnished with a large wooden bowl, of about two feet in diameter, and one foot in depth, and have a leathern bag tied before them for the reception of the particles of gold dust which they may collect. The localities generally chosen for these washings are those parts of the river where the current is not rapid, and where it makes numerous bends, and forms deep holes. The large stones and upper layers of sand are first removed, and the bowl is then filled with the deeper and older gravel of the river, which is shaken and washed, and the stones and sand on the top scraped off, until the grains of gold alone remain at the bottom of the vessel. This residue is now moistened by a little water thrown on by the hand, and washed into the leathern bag before described. Instead of operating in this way, the auriferous sands are sometimes washed in long shallow troughs, the bottoms of which are covered with skins tanned with the hair on, and of which the hairy side is placed upwards. Instead of employing skins for this purpose, coarse baize is sometimes used; but in either case the moveable lining is at short intervals removed from the case, and beaten over a tank containing about two feet of water, and afterwards washed in it until all the adhering gold is disentangled, after which they are again replaced in the troughs. To prevent theft, these tanks are carefully locked up during the night, and when they have become full their contents are cautiously washed in hand-bowls until nothing but the gold remains, mixed with a greater or less amount of peroxide of iron.

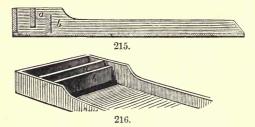
The residue, whilst in a damp state, is now intimately mixed with a small quantity of metallic mercury, which takes up the particles of gold, and leaves the oxide of iron in an uncombined state. The pasty amalgam, after being separated from the oxide of iron, is now carefully folded in a closely-wove cloth, and wrung until about one-half of the quicksilver originally added has been separated in a free state. What remains is afterwards put into a small metallic dish, and covered by a few green leaves, and then placed over a charcoal fire, where it is stirred with an iron rod. When the leaves have become much parched, they are replaced by a succession of fresh ones, and from these, at the close of the operation, a considerable quantity of condensed mercury is obtained. The gold, of a dirty brown colour, and still containing a certain proportion of mercury, remains at the bottom of the dish.

In the Ural districts, from whence, notwithstanding the extreme poverty of the auriferous sands there found, the chief annual supply of gold has to within a very recent period been obtained, the methods of washing employed are very various. In some cases the auriferous sands are thrown into boxes, of which the bottoms are composed of thin sheet iron, pierced with numerous small holes; these are placed immediately under a considerable fall of water, and the mineral kept constantly agitated by workmen, who keep it stirred with shovels. By this treatment the finer particles are carried through the apertures in the bottoms of the boxes, and fall on a series of sloping tables, on which the workmen constantly brush the ore from the foot to the head of the arrangement with a small heath broom, and there the particles of gold and other heavy substances accumulate. The sand, after being thus concentrated and separated from the lighter matters, is further enriched by a second washing on a series of tables of smaller dimensions. The titaniferous iron, together with the magnetic oxide of iron, which is invariably present, is now partially separated by the aid of a powerful magnetic bar, and the residue subsequently fused in a graphite crucible, with a mixture of carbonate of soda and nitre, to which borax is sometimes added. From its greater density, the gold collects at the bottom, whilst its surface is covered by a more or less liquid slag, which retains numerous globules of metallic gold. This scoria is afterwards stamped and washed, and the rich slimes thus obtained are subsequently fused in a cupola furnace, together with lead ores; the auriferous lead thus obtained is ultimately treated by cupellation. Instead of washing the auriferous sands by means of wooden vessels with perforated iron bottoms, many of the workings for gold in the Ural mountains are conducted by the aid of the washing cylinder represented fig. 214. This machine consists of a cylinder of sheet iron, A, pierced with holes of about half an inch in diameter, and strengthened on the inside by a strong iron trellis. The cone, which may be about 8 feet in length, and has a mean diameter of about 3 feet 6 inches, is larger at one extremity than at the other, and is fixed on a spindle capable of being set in rapid motion by means of a train of wheels, worked by the horse gin, B, securely fastened to the ground by strong oak or other sleepers. The auriferous sands to be treated are brought in waggons running on iron rails to the hopper, c, from whence they fall into the moveable cylinder through the aperture formed by its smaller circumference. At the back of the arrangement is a double pump, D, set in motion by a crank on the shaft, which communicates motion from the gin, B, to the cylinder, A. This pump raises water from a well or some other convenient source, to the cistern, E, from which it is conducted by means of four iron pipes into the cylinder, A; these pipes enter the cavity of the drum through the two open ends, and are so arranged with regard to length as to afford a nearly equal supply of water throughout its whole capacity. When set in motion, the perforated cylinder makes from thirty to thirty-five revolutions in a minute, and consequently throws, by its centrifugal action, the water and finer particles of sand and gravel through the numerous perforations which it contains; whilst the pebbles and other fragments, which are of too large a size to pass through the holes, are carried off through the larger end of the cylinder, and there fall into a box not shown in the drawing. This receptacle will contain any nuggets which may have been present in the sands; and as, by passing through the cylinder, they will have been washed perfectly clean, they may now be readily seen and picked out. The sand and water, after having escaped through the apertures in the drum, fall on the inclined platform, F, which is provided with numerous horizontal bars, for the purpose of separating the heavier from the lighter portions of ore. From this platform the current flows on to the concave table, H, also provided with checks, in the form of wooden bars, nailed across it at distances of about 3 feet from each other.



The sands which have arrived at this part of the table are now kept constantly agitated by the wooden pendulums, I, I', provided at their lower extremities with frames made to suit the concavity of the table, and fitted with flattened teeth, like those used in some kinds of farming implements. These pendulums are made to swing by means of the rods,  $\kappa$ , driven by the crank,  $\alpha$ , and are so arranged as to move constantly in opposite directions. In this way the operation is continued, until a considerable accumulation of rich auriferous sand has taken place at the upper part of the tables, where, being retained by the horizontal slips of wood, it remains; whilst the lighter matters are carried off by the current of water to the lower end of the table, H, from whence they are either made to pass over a fresh series of tables, or if, as is usually the case, they are found to be sufficiently impoverished, they are allowed to run entirely away.

When a sufficient accumulation of rich auriferous sand, called grey schlich, has taken place behind the various check-boards nailed across the tables, it is carefully collected for the purpose of further concentration on small inclined tables. These consist of wooden troughs, figs 215, 216, of about 9 feet in length, and 3 feet 6 inches in breadth, provided with a head board, as shown in the sketch, fig. 215, and in which a constant and very equal flow of water is obtained, by the use of the boards, a, b. The schlich to be washed has to be placed at b, and an equal and very light (gentle) current of water allowed to flow over its surface,



whilst it is being constantly moved by a small wooden rake, or heath broom, towards the head of the arrangement. By skilful treatment in these tables, or fine washing as it is called, the gold may be almost entirely separated from the associated sterile matters, and may then be treated either by amalgamation or direct fusion. The cylindrical machine above described is, when driven by three bullocks, or two good horses, capable of passing 120 tons of alluvial sand in the course of an ordinary working-day of ten hours. The sand is thus concentrated to about two tons, which are washed, as before described, on small inclined tables. With a small machine of this description, one man may, without aid, readily wash at least ten tons of sand and gravel per day. Nothing need be said of the efficiency and economy of these machines, when it is stated that the sands of the Ural rarely contain above eighty grains of gold to the ton of mineral, and are nevertheless advantageously treated by this and various similar, though slightly modified arrangements.

The gold-mining associations hitherto carried on in Australia have for the most part been conducted on a very rude scale, but many extensive and well-appointed establishments have commenced their operations in different localities. The vessels at first made use of for the purpose of washing were either tin pans or closely-wove Indian baskets, although a rude machine, known by the name of a cradle, was also extensively used. This consists of a trough, six or eight feet in length, with a rounded bottom, across which two pieces of wood, serving as rockers, are nailed. At the head of this arrangement is placed a coarse grate, on which the sand to be washed is charged, and thereby separated from the coarser particles, which are retained on the meshes. To work this machine four men are required : one breaks the ground and collects the auriferous sand, another carries it to the washing place and deposits it on the grating, a third violently rocks the trough, whilst the fourth attends to the supply of water, and the regular washing of the ore. The coarser gravel and large stones are prevented from entering the trough by the grating at the head; the earthy matters are washed off by the current of water escaping by the lower end, which is left open for that purpose, whilst the gold, mixed with a small quantity of ferruginous earth, collects on the higher part of the trough, which has an inclination of about four inches in its whole length.

At this stage of the operation, the gold, mixed with the ferruginous particles, is drawn off through an aperture made in the bottom into a pan placed below, and after having been dried in the sun the lighter portions are removed by strongly blowing on the mixture. In spite, however, of these very rude contrivances, a company of four men thus employed, have not unfrequently realised a profit of a hundred dollars per diem.

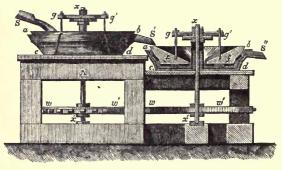
The machinery recently put up, and at present in course of erection by the several companies by whom gold-mining has been undertaken, includes crushing-rollers, stamping-mills, jigging machines, sleeping tables, and all the other appurtenances of regular metallurgic establishments, and consequently results more satisfactory than those already obtained may yet be anticipated.

When gold exists in veins which at the same time produce other metals, such as silver, lead, or copper, the ore is at once treated for these metals, with which the gold combines to form an alloy, and from which it is afterwards readily separated. If, in addition to

#### GOLD.

gold, the mineral also contains lead, auriferous metallic lead is obtained; this is subsequently treated for the precious metal by cupellation. When copper ores contain gold, either the black copper obtained by its metallurgic treatment is subjected to liquation, or the matts produced by its direct fusion are made to undergo a process of amalgamation. The separation of the gold and silver is afterwards effected by a process called *parting*, which will shortly be described.

In the Tyrol, where small quantities of gold are extracted by amalgamation from an auriferous iron pyrites, the operation is conducted in a kind of mill, of which fig. 217 is a representation. A number of these machines are so arranged one above another that the products escaping from the first may flow into the second, and so on throughout the whole length of the series. The pyrites to be treated is first reduced by stamping-mills to the state of fine powder, and whilst held in suspension by a stream of water is conducted into the upper mill by the spout, s, and flowing



217.

through it passes by the pipe, s', into the second, from which it is subsequently conducted into other mills, not shown in the woodcut. The fixed part of these mills consists of a cast iron capsule,  $a \ b \ c \ d$ , fastened by screws to the top of a strong wooden table, A. The centre of this casting is furnished with a tubulature traversed by the rotating axis,  $x \ x'$ , and set in motion by the toothed wheel,  $w \ w'$ . The upper and moveable part of the arrangement,  $f \ f$ , (shown in section in the right hand figure,) is composed of hard wood, and fixed to the upright spindle by the iron collar,  $g \ g'$ . This moveable part of the mill has externally the same form as the internal cavity of the fixed iron casting, from the surfaces of which it works, at the distance of about half an inch; it is also furnished with several raised ribs nailed to its under side, and which come almost in contact with the bottom of the iron pan.

The upper surface of this wooden muller is hollowed out in the form of a funnel, into which is conducted the liquid slime, which quickly penetrates into the space remaining between the two surfaces of the upper and lower parts, and then flows over the sides of the basin by the spout placed there for that purpose. On the bottom of the iron pan is placed about half a hundred weight of mercury, which forms a stratum of rather more than half an inch in thickness, and with which, when the machine is set in motion, the pounded mineral is constantly agitated by the projections nailed to the bottom of the revolving block of wood. The spangles of gold are thus instantly dissolved the moment they come in contact with the mercury, whilst those which escape combination in the first amalgamation are arrested by the others following in the same series. After this apparatus has been at work during four or five consecutive weeks, the mercury is drawn off and filtered through a piece of chamois skin, for the purpose of obtaining the solid amalgam. This usually contains about onethird of its weight of pure gold, which is obtained by a process of distillation, by which the quicksilver is eliminated, and the gold remains behind in a state of minute division.

#### ESTIMATION OF GOLD -ASSAY OF AURIFEROUS ORES.

Estimation .- For analytical purposes, gold is invariably estimated in the metallic state, in which form it is frequently precipitated from its solutions by the addition of sulphate of protoxide of iron. In order that this operation should succeed, it is, however, important that the liquor be acidulated by hydrochloric acid previous to the addition of the salt of iron, as by this means the peroxide of that metal formed, and which would otherwise be precipitated, is held in solution. The presence of nitric acid also prevents the accurate estimation of this metal, and consequently, whenever that body is present in the solution, it must be evaporated nearly to dryness, with the addition of hydrochloric acid, before the sulphate of iron is added. The metal thus precipitated is collected on a filter, and heated to redness in a porcelain crucible previous to being weighed. The separation of gold from the other metals is sometimes founded on its insolubility in nitric acid, and at others on its property of being precipitated from its solutions by oxalic acid and sulphate of iron.

When sulphide of gold, precipitated by a current of hydrosulphuric acid, is heated to redness, the sulphur is expelled, and pure metallic gold remains in the crucible.

Assay of Auriferons Ores .---- Minerals containing gold are assayed in precisely the same way as the corresponding ores of silver, but as these bodies are usually very poor, it becomes necessary to operate on a larger quantity of the substance to be examined. When these compounds contain oxide of lead they may be conveniently fused with a proper quantity of black flux : if, instead of containing oxide of lead, they consist of other oxidised bodies, but are free from this metal, the assay may be advantageously conducted by the addition of a mixture of litharge and black flux; when chiefly composed of siliceous and earthy matters mixed with rich oxidisable substances, as mispickel, or iron or copper pyrites, their fusion may be effected by the use of litharge only; and lastly, when these substances so preponderate as to yield too large a button of lead for convenient cupellation, a mixture of litharge and nitre may be used with advantage. It is, however, necessary to remember, that when any of these compounds contain sulphur, it is of the greatest importance that the whole of it should be entirely removed during the process of assaying, as otherwise, and particularly in presence of alkaline sulphides, a large quantity of the gold would enter into combination with the slags in such a way as not to be separated from them either by lead or any other metal.

**Cupellation**.—The buttons of alloy thus obtained are afterwards cupelled, with the precautions enumerated when treating of the assay of the alloys of silver, although, when gold is the metal sought for, the process is in a slight degree varied.

When the resulting button merely consists of an alloy of lead and gold, together with a small admixture of one or more oxidisable metals, its cupellation presents even less difficulty than in the case of the alloys of lead and silver, because in the first place the resulting button of gold is not only less volatile than that of silver, and consequently may be exposed to a greater heat, but less loss is also experienced at high temperatures by absorption into the substance of the cupel.

When, in addition to gold and lead, the button obtained by assay likewise contains copper, it must be cupelled like the similar alloys of silver, but as copper possesses a much greater affinity for gold than it has for silver, a proportionately large addition of lead must be made in order to insure the production of a perfectly pure button on the test. This proportion varies in accordance with the composition of the alloy operated on, as shown in the following tabular arrangement, which indicates the total amount of lead to be added to various alloys of gold and copper in order to obtain the former metal in a perfectly pure state.<sup>1</sup>

<sup>1</sup> Regnault.

Proportion of gold contained in the alloy.					Quantity of lead necessary to completely remove the copper by Cupellation.			
1000 thousandths				3.		1	part	
900	"					10	,,	
800	,,					16	,,	
700	37					22	"	
600	,,					24	33	
500	22					26	"	
400)								
300								
200 }	22					34	99	
100								
50								

Ores containing Gold, Copper, and Silver.-When, as is frequently the case, the button obtained by the fusion of the ores contains, in addition to lead, copper, and gold, a certain proportion of silver, it must be cupelled at a moderate temperature, and if necessary an additional quantity of silver added. By operating in this way, the button obtained on the cupel consists of an alloy of silver and gold, which is afterwards treated by an excess of nitric acid: this effects the solution of the silver, and leaves the gold untouched in the form of a brown powder, in the bottom of the flask in which the experiment has been conducted. In order, however, to obtain perfectly exact results, it is necessary that a certain relation should exist between the amount of the two metals of which the alloy is composed, since if the silver be not present in sufficient quantity, the mixture is not completely attacked by the nitric acid; whilst on the other hand, when too large a proportion of this metal is added, the gold remains in a pulverulent form, which renders its collection for the purpose of weighing extremely difficult.

**Forting.**—This operation, which has received the name of *parting*, is found to succeed most perfectly when the alloy contains a little less than three parts of silver to one of gold; and therefore, in all cases where great exactitude is required, the addition of silver must be so managed as to agree as closely as possible with this proportion. If the alloy contain less than two and a half parts of silver to one of gold, the solution of the silver cannot be completely effected, as in this case some of its particles are so enveloped in gold as to resist the action of the strongest acid.

The operation of adding the proper amount of silver to an alloy to reduce it to the right standard for the process of parting, is called *inquartation*. The quantity of silver necessary for this purpose is estimated in accordance with the approximative composition of the alloy produced by direct cupellation of the button obtained by assay, which may be judged of either by the touchstone, as will be presently described, or, in many instances, by a simple inspection of its colour and hardness.

The inquartated button when obtained, should be carefully flattened with a polished hammer on a steel anvil, and afterwards attacked in a small flask or large test-tube by nitric acid of specific gravity 1.15. After having been boiled for about ten minutes with acid of this strength, the liquid is carefully poured off, and the residue heated to ebullition during a quarter of an hour in acid of the specific gravity 1.26. At the expiration of this time the acid is carefully poured off, and the residual gold, after being completely washed with distilled water, is transferred to a thin porcelain capsule, from which the water is partially removed by a pipette, and the remainder evaporated by exposure in a waterbath. When perfectly freed from moisture, the pulverulent gold may be either weighed directly in the capsule in which it has been dried, or be folded in a little poor lead foil and again passed to the cupel, so as to obtain it in the form of a pure metallic globule.

Assay of Artificial Alloys.-As in this case the standard of the metal operated on is in most instances approximatively known without having recourse to any preliminary investigation, the operation usually commences by fusing the alloy in a cupel with about twice its weight of poor lead, and then adding the amount of silver or fine gold necessary to bring the mixture to the proper composition. After having in this way obtained a button by cupellation, it is first flattened on an anvil, and afterwards annealed by being again heated to redness in the muffle, when it is drawn out into the form of a long strip, by being repeatedly passed between the rollers of a small flatting-mill. During the progress of this operation the metal requires to be a second time annealed, and when sufficiently reduced in thickness should represent a. metallic ribbon of a quarter of an inch in width and two and a half inches in length. A convenient weight of alloy to operate on is 25 grains. In laminating the cupelled button, it is, however, necessary that it should be reduced to a suitable thickness, so that on the one hand the silver may be completely dissolved, whilst on the other, if the lamination be carried too far, the gold remaining after the operation will not possess sufficient coherence to admit of its being conveniently removed and passed to the muffle.

The strip of alloy thus prepared is now wound in the form of a spiral around a piece of glass rod or the barrel of a quill-pen, from

which it is removed to a small glass mattrass, capable of holding about three ounces of water, which, with the tongs used for holding it, is represented fig. 218. One and a half ounce of nitric acid of specific gravity 1.15 is now added, and the whole exposed to the tempera-



ture of ebullition during twenty minutes, when the first liquor is carefully poured off and replaced by the same quantity of acid, having a specific gravity of 1.26: with this the residue is briskly boiled for another ten minutes, after which it is poured off and the remaining gold carefully washed. The flask is now entirely filled with distilled water, and after covering the neck with the thumb, so as to prevent the escape of any of the liquid, it is so inclined as to allow the cornet of spongy gold, which retains the form of the original alloy, to slowly descend without breaking to the neck of the mattrass. The metallic spiral is now carefully placed in a small earthen crucible, from which the water is poured off, and which is afterwards heated in the muffle to bright redness.

In these estimations it is of importance that the alloy should not be immediately attacked by the stronger acid, as in this case the gold would, by the rapid action on the silver, be divided in the form of a fine powder, whilst if on the other hand the acid of specific gravity 1.15 only were employed, the whole of the silver could not be completely separated from the original gold sponge. When the attack has been conducted with proper care, the gold remains in the form of a friable brown sponge, having very nearly the same dimensions as the original spiral of alloy: on heating this, however, as before described, it very sensibly contracts, and at the same time acquires the colour and consistence of ordinary malleable gold. The results thus obtained differ from one-quarter to one-half thousandth from the actual truth, and are, therefore, sufficiently exact for every commercial purpose.

Determination by the Touchstone.—The methods of assay already described, although succeeding perfectly for the determination of the value of bullion and other unmanufactured products, cannot be conveniently applied to the examination of jewellery, which would be required to be destroyed, in order to ascertain its composition, and consequently a method is employed by which its standard is readily determined to within 1 per cent. of the truth, whilst the most delicately chased article is in no way disfigured by the trial. This process essentially consists in rubbing some convenient part of the object to be examined on a hard siliceous stone of a black colour, on which it thus leaves distinct metallic traces : from the aspect of these marks, and their behaviour when treated with nitric acid or a weak solution of aqua regia, the assayer judges of the gold subjected to examination. The material employed for this purpose, and which is generally known by the name of *touchstone*, is a coarse-grained species of quartz, coloured by bituminous matter, and which was anciently brought for this purpose from Lydia, although stones of equally good quality are now obtained in Saxony, Bohemia, and numerous other localities.

In order to be enabled to judge of the value of an alloy from the nature of the mark left by it on the surface of the stone, the assayer is furnished with a series of small bars, or touch-needles, formed of alloys of copper and gold, of which the composition is accurately determined.

The trace left on the stone by the alloy to be examined, is successively compared, both before and after the action of an acid, with the different marks obtained from these needles, and it is supposed to possess a similar composition to the needle whose mark agrees most closely with it under both these circumstances. The acid most commonly employed for this purpose is nitric acid of sp. gr. 1.26, to which about 2 per cent. of hydrochloric acid has been added. In making these assays, the first streak obtained on the stone cannot be employed to ascertain the composition of the object examined, as the surface of jewellery is invariably rendered, by the process of colouring, of a higher standard than that of the alloy of which it is throughout composed. For this reason, therefore, the object must be passed once or twice over the surface of the stone, in order to remove the superficial coating of richer alloy, before making the streak from the comparison of which with those of the needles the commercial value of the mixture is to be determined. This method, although affording much less accurate results than those obtained by inquartation, is nevertheless for many purposes sufficiently exact.

When, in addition to copper, gold, and silver, the alloy also contains a certain proportion of platinum, the separation by cupellation of the oxidisable metals, and especially copper, is rendered extremely difficult. In this case it is necessary that the silver present should be at least double the united weights of the gold and platinum contained in the alloy, and that it should be cupelled at a very high temperature with the addition of large quantities of lead. The button thus obtained is afterwards to be treated with nitric acid in the usual way, when the presence of so large a

## REFINING THE PRECIOUS METALS.

proportion of silver determines the solution of the platinum, whilst the gold remains untouched in the bottom of the flask, and is collected and weighed as already described.

# REFINING THE PRECIOUS METALS—PARTING ON THE LARGE SCALE.

When the separation of gold from silver is conducted on an extensive scale, the use of nitric acid would be attended with considerable expense, and could therefore only be resorted to when the proportion of the more valuable metal is considerable. This difficulty is, however, entirely obviated by the employment of sulphuric acid, although it is necessary, in order that the alloy be completely attacked, that it should not contain more than 20 per cent. of gold, and from the slight solubility of sulphate of copper in strong sulphuric acid it is also of importance that it should not contain much beyond 10 per cent. of copper.

The alloy, after the additions necessary to bring it to about this standard have been made, is fused either in large crucibles or in a small reverberatory furnace, and granulated by being thrown, while still in a liquid state, into vessels containing cold water. The granulated mixture is now placed in large cast iron boilers, into which are thrown 21 times its weight of strong sulphuric acid of sp. gr. 1.848, and the whole is at once heated to ebullition by a fire placed beneath the pans. The quantity of alloy treated in each vessel varies from 4 to 6 cwts., and to prevent the evolution of noxious gases into the laboratory, a leaden dome, connected with a well-drawing chimney, is placed over them during the whole time the attack is being made. The strong sulphuric acid under these circumstances is rapidly decomposed, sulphate of silver is formed, and sulphurous acid gas is evolved; this, for the sake of economy, is frequently conducted into a sulphuric acid chamber, where it again becomes oxidised, and is therefore fitted to be employed in a repetition of the same process. At the expiration of four hours the attack is completed, and at this stage of the operation is added a certain quantity of sulphuric acid of the sp. gr. 1.69, obtained by the concentration of the acid mother liquors remaining after the crystallisation of the sulphate of copper produced during the precipitation of the metallic silver, as will presently be described.

The liquors are now again made to boil during a few minutes, when the fire is withdrawn from beneath the pans, and the liquors are allowed to stand, in order that the finely divided gold may become deposited on the bottom. When this has taken place, and the supernatant liquor has become nearly clear, it is drawn off by a syphon, while still hot, into leaden evaporators partially filled with the mother liquors remaining from the crystallisation of the sulphate of copper. These are heated by a series of steam-pipes until the whole of the sulphate of silver which at first falls down is redissolved, when a further precipitate of gold is obtained, and the liquor again syphoned into another series of evaporators, in which are suspended a number of copper bars, by which the silver is rapidly precipitated in the form of a crystalline powder. In the course of a few hours the last traces of silver are by this means completely removed, and the metallic deposit, after being carefully washed, is compressed by a powerful hydraulic ram into the form of solid rectangular prisms.

These, when dry, are fused in large earthen crucibles, and cast into ingots. The silver thus obtained contains from three to five thousandths of copper.

The pulverulent gold obtained by this first attack still contains a considerable quantity of silver, and is therefore again subjected to the action of strong sulphuric acid in platinum vessels heated from a fire placed beneath.

When not sufficiently purified by this second ebullition in strong acid, it is subjected to a third operation of a similar kind, and afterwards fused and run into bars, which commonly contain about 99.5 per cent. of pure gold.

The solution of sulphate of copper produced during the precipitation of the silver by copper bars is evaporated in a shallow cistern lined with lead, and heated by a series of steam-pipes laid in zig-zag across the bottom. When the liquors have in this way been concentrated to sp. gr. 1.40, they are syphoned off into large tubs lined with lead and bound with copper hoops, as from the readiness with which sulphate of copper acts on iron, bands of this metal would be rapidly corroded by any of the liquor accidentally spilt over the sides of the vessels. After having been filled, these tubs are closely covered to prevent their too rapid cooling, and after the expiration of about five days the mother liquors are drawn off, and the crystals of sulphate of copper adhering to the sides carefully removed. These mother liquors, when again concentrated, yield a further supply of crystallised salt, after which they are set aside to be employed in place of sulphuric acid in the first stage of the operation, as already described.

When sulphate of copper of very superior quality is required, the crystals first obtained are sometimes subjected to a second crystallisation, but in the majority of cases they are merely washed on a wicker sieve, and after being allowed to drain in a large leaden cullender, are packed in strong casks for the market. From the great economy with which this process is conducted, and the present low price of sulphuric acid, it admits of being advantageously applied to the refining of silver containing 0.005 only of gold. When an alloy chiefly consists of copper, and contains at most from twenty to thirty per cent. of the precious metals, the parting is not attempted until a portion of the copper has been oxidised by roasting in a reverberatory furnace.

The granulated alloy, after having been thus treated, is acted on by weak sulphuric acid, by which the oxide of copper is alone dissolved; and when the mixture has in this way been enriched until it contains from 50 to 60 per cent. of gold and silver, it is subjected to the usual process of refining by strong sulphuric acid. This method of enriching the alloy by the oxidation of its copper was first employed by M. Lebel, the proprietor of the factory of Belleville, near Paris, who for many years employed it with great success: it was also for some time practised at Freyberg for the purpose of separating the copper from silver obtained by amalgamation; but as the alloy there treated contained small quantities of several other metals besides copper, the fine silver obtained was found to be rather brittle, and for this reason the process was ultimately abandoned. During the time it was employed, the metal to be refined was subjected to three successive roastings and attacks, and in this way silver containing only four thousandths of impurity was obtained.

Alloys of Gold. Gold, like silver, is seldom employed for the purposes of the arts in a pure state, but is alloyed with a small quantity either of silver or copper, by which its hardness, as well as its fusibility, is considerably increased.

In this country the standard of the alloys of gold is calculated in fractions of unity expressed in carats. Unity is supposed to be divided into 24, while each carat is itself subdivided into 32 thirty-secondths, so that unity may be considered as made up of 768 thirty-secondths of a carat.

In this way the gold coinage of England is said to have a standard of 22 carats, or, in other words, it consists of an alloy in which in every 24 parts there are 22 parts of fine gold and 2 of alloy. The common standard for jewellery is 18 carats, and on articles made of this alloy the Hall mark of the Goldsmiths' Company is generally affixed; jewellery of a less standard than 18 carats does not, however, receive the mark of the Company, and it therefore not unfrequently happens that chains, &c., sold as gold do not contain even fifty per cent. of that metal.

The colouring, as it is called, of jewellery, is effected by externally dissolving out the copper with which it is alloyed, and thereby exposing a superficial facing of fine gold. To produce this effect, the object to be coloured is first heated nearly to redness in a gas jet or spirit lamp, and then plunged into a weak solution of nitric acid, by which the copper on its surface is removed. The same effect is also produced by placing for a few minutes the object to be coloured in a paste composed of a mixture of alum, common salt, and saltpetre. In this case the chlorine evolved from the mixture dissolves out the copper, and leaves the object with a surface which is readily brightened by polishing, and when finished presents all the depth of colour possessed by pure gold.

The gilding of metallic ornaments is either performed by rubbing their surfaces, rendered perfectly clean by immersion in dilute nitric or sulphuric acid, with an amalgam of gold and mercury, and then expelling the latter metal by heat, and subsequently burnishing down the deposited gold; or, when the object to be gilt is entirely composed of copper, it may be made to receive a covering of gold by being first cleaned and amalgamated by being dipped into a solution of nitrate of mercury, and then, after being carefully washed, placed in a vessel containing a boiling solution of chloride of gold in an alkaline carbonate. The objects gilt by this method are afterwards coloured by dipping them into water containing a mixture of nitre, sulphate of zinc, and green vitriol; they are then dried at a charcoal fire, and subsequently washed in clean water. These, and all the other processes by which gilding was formerly effected, have, however, within a few years, become in a great measure superseded by the various processes of electro-gilding, which consists in depositing from its solutions by electric agency a layer of gold of any desired thickness.

The solution most commonly employed for this purpose is evanide of potassium, containing cyanide of gold; the subject to be gilt is attached by a metallic wire to the negative pole of the arrangement, whilst in connection with the positive is a piece of pure gold, which is dissolved in proportion as the metal is deposited on the object to be gilt. By this means, therefore, the thickness of the coating is not only entirely under the command of the operator, but the strength of the solution is also constantly kept up at the expense of the ingot of gold in communication with the positive pole.

## PLATINUM.

(593)

## Equiv. = 98.68. Density = 20.98.

PLATINUM is a metal of a greyish-white colour, capable of receiving a very high degree of polish. When perfectly pure it is extremely malleable and ductile, but the presence of a very small amount of foreign matter is sufficient to destroy these properties, and to render it both dull and brittle. The tenacity of pure platinum is nearly equal to that of iron, but ordinary commercial specimens almost invariably contain a certain proportion of iridium, by the presence of which this property is considerably impaired. This metal is infusible when exposed to the strongest heat of a wind furnace, but melts before the flame of the oxy-hydrogen blowpipe, or between the charcoal poles of a powerful galvanic battery. Like iron it yields to the hammer, and admits of being forged and welded at a white heat.

Platinum is not attacked by any of the simple acids. The strongest nitric, hydrochloric, or sulphuric acid is entirely without action on this metal, but when alloyed with a sufficient amount of silver it is readily dissolved by the first-named menstruum. By aqua regia it is dissolved with the formation of a bichloride of the metal.

Platinum is readily attacked by the caustic alkalies at a red heat, and particularly by lithia, but is in no way affected by the alkaline carbonates, even when exposed to their action at a very elevated temperature. A mixture of nitre and caustic potash produces this effect with much greater rapidity than the alkalies alone, and ordinary laminated platinum is found, when heated in presence of arsenic, sulphur, and phosphorus, rapidly to lose its malleability and ductility. When these bodies are brought at a high temperature in contact with platinum in a high state of division, combination readily takes place, and fusible and extremely brittle compounds are the result. A mixture of silica and carbon produces a similar effect on this metal, and for this reason platinum crucibles which have been frequently ignited in an open fre gradually become rough on the exterior and quickly lose their flexibility. For this reason platinum vessels should never be exposed to the direct action of a furnace, but be enclosed in an earthen crucible containing a little magnesia or caustic lime.

Platinum, when in an extremely divided state, possesses certain remarkable properties, which render it of frequent employment in the chemical laboratory. When in this form, it is known by the name of platinum-black, and has then the property of condensing to a most extraordinary extent the gases in which it is placed. In this way platinum-black, which has for some time been exposed to an atmosphere of oxygen, will condense around it several hundred times its volume of that gas, and when brought into contact with certain inflammable bodies causes their instantaneous ignition. If, for example, a drop of absolute alcohol be let fall upon a small lump of this substance, which has thus been exposed in the presence of oxygen gas, it is at once inflamed, and the whole mass of the metal instantly becomes incandescent.

Platinum, in an extreme state of division, may be prepared in various ways. The most common method is by boiling a solution of bichloride of platinum Pt Cl<sub>2</sub> with carbonate of soda and sugar. In this case a formation of chloride of sodium takes place, the platinum is precipitated in the metallic state, and the oxygen abandoned by the soda decomposes a portion of the sugar, which is thus converted into water, and carbonic acid, which escapes during ebullition. Platinum-black may also be made by dissolving protochloride of platinum, Pt Cl, in caustic potash, making the liquid boil violently, and gradually adding a small portion of alcohol to the solution. Rapid evolution of carbonic acid now takes place, and the metal is precipitated in a state of extreme division. The same result is likewise obtained by decomposing sulphate of platinum by the aid of heat and strong alcohol. Platinum prepared by one of the foregoing processes is of constant employment in eudiometrical experiments.

Platinum was not imported into Europe until the middle of the last century, although known long previous to that time in America under the name of *platina*, which signifies in Spanish *little silver*, and was even then, from the great difficulty experienced in working it, of comparatively little value. The platinum of commerce is never absolutely pure, but contains a greater or less proportion of iridium and other metals, by which its malleability is considerably impaired. To obtain pure platinum, ordinary chippings of that metal are dissolved in aqua regia, and to the filtered liquor is added chloride of potassium as long as a yellow crystalline precipitate continues to be formed. The precipitate, which is a double chloride of platinum and potassium, is very slightly soluble in water, but contains in most instances a small portion of the double chloride of iridium and potassium. To the precipitate thus obtained is added about its own weight of carbonate of potash, and the mixture, after being properly incorporated, is heated to redness in an earthen crucible. On being thus treated, the chloride of platinum gives up its chlorine to the potassium of the carbonate of potash, and the metal itself is isolated, whilst the carbonic acid, together with oxygen gas, escapes from the crucible. The chloride of iridium is at the same time decomposed, but the metal not being reduced to the metallic state, oxide of iridium remains. The calcined mass is now treated with hot water, by which the alkaline salts are readily removed; whilst the metallic residue, after being properly washed, is attacked by dilute aqua regia, which dissolves the platinum, whilst the oxide of iridium remains untouched. Sal-ammoniac (chloride of ammonium) is now added to the platinum solution, by which the double chloride of platinum and ammonium, having the formula PtCl<sub>2</sub> + NH<sub>4</sub>Cl, is formed and precipitated. This, after being carefully washed in distilled water, is decomposed by being heated to redness, and the spongy mass remaining in the crucible may readily be compressed into the solid form by being subjected to great pressure when strongly heated.

## SOURCES OF PLATINUM.

This metal is invariably found in a native state, and occurs in alluvial deposits similar to those from which gold is obtained: the sands producing platinum are principally discovered in open valleys traversing serpentine rocks. It generally presents the appearance of small flattened grains, of a greyish-white colour, approaching that of tarnished steel. These grains are commonly flattened, and appear to have been polished by friction against other hard bodies. Their size varies from linseed to that of hempseed, but a few fragments of much larger dimensions have occasionally been discovered. One piece brought from Choco in Peru, by Humboldt, and presented to the Cabinet of Berlin, weighs 850 grains, or nearly two ounces avoirdupois.

The Royal Museum of Madrid possesses a specimen found in 1844 in the gold mine of Condota, in South America, which is as large as a turkey's egg, and weighs 7,600 grains.

A specimen of this metal was found in the year 1827 in the Ural mountains, not far from the Demidoff mines, which weighed 11:57 lbs. troy. The largest specimen yet discovered weighs 21 lbs. troy, and is in the cabinet of Count Demidoff.

The grains of platinum are generally far from pure, and are commonly combined with osmium, iridium, palladium, rhodium,

## PLATINUM.

and ruthenium, besides gold, silver, iron, and copper; they are also frequently associated with various heavy minerals, such as the magnetic oxide of iron, titaniferous iron, chrome iron ore, and iron pyrites.

Three specimens of native platinum yielded to Berzelius the following results :---

in su	rom the U grains; i				n Columbia : nall grains.
Platinum	78.94	73.58			84.30
Rhodium	0.86	1.15			3.46
Palladium	0.28	0.30			1.06
Iridium	4.97	2.35			1.46
Osmium	1.96	,,			1.03
Iron .	11.04	12.98			5.31
Copper .	0.20	2.30			0.74
		PPrint, Carriero and			
	98.75	92.66			97.36

This metal was first discovered by Ulloa, a Spanish traveller, in the alluvial deposits of Choco and Barbacoa in South America. It has since been found in the Ural mountains, in the island of Borneo, in the sands of the Rhine, in those of the Jocky in St. Domingo, and in the gold regions of Brazil.

The gold-washings in Peru that furnish most platinum are those which are situated between the second and sixth degrees of South latitude. Among these may be mentioned the mines of Condota in the province of Novita; those of Santa Rita in Viroviro; of Santa Lucia, and the ravines of Iro and Apoto, between Novita and Taddo. The deposit of platinum here occurs in the alluvial soil, at the depth of about 20 feet from the surface.

The grains of platinum are separated from gold either by handpicking or amalgamation. From an apprehension that this metal might be employed for the purpose of debasing gold, it was formerly thrown into the rivers with a view of preventing fraud, and through this, large quantities of this valuable metal have been entirely lost. The platinum grains which are found in the river Jocky, near the mountains of Sibao, are extremely brilliant, and intermixed with a siliceous sand, which is frequently ferruginous.

The largest proportion of the platinum at present used is obtained from the Ural districts of Nischne, Tagilsk, and Goroblagodat. It here, as elsewhere, occurs in alluvial beds; but the course of the platiniferous alluvium, which is extremely productive, has been traced for a considerable extent up Mount la Martiane, which consists of a crystalline rock, from the disintegration of which the sandy deposit is obtained.

Russia annually affords about 80 cwts. of this metal, which is about ten times the amount of the united products of Brazil, Borneo, St. Domingo, and Columbia.

The production of Borneo is estimated at 600 lbs. per annum.

# ESTIMATION OF PLATINUM, AND ITS SEPARATION FROM OTHER METALS.

This metal is, for the purposes of analysis, weighed either in the metallic state, or in the form of the double chloride of platinum and ammonium, Pt  $Cl_2$ +NH<sub>4</sub>Cl, which is collected on a filter of known weight, and carefully dried at a temperature of 212° Fahr.

When platinum exists in a solution in the form of chloride, the liquor is first concentrated by evaporation, and subsequently mixed with about twice its volume of pure alcohol.

Solution of chloride of ammonium is now added in excess, and the liquor again concentrated by evaporation in a water-bath; by this means the double chloride is completely precipitated, and after being carefully washed in strong alcohol, is dried, either under the exhausted receiver of an air-pump, or at a very moderate temperature in a water-bath. From the weight of double salt thus obtained, the per-centage of platinum is readily deduced, as every 100 parts of the former correspond to 44-23 parts of metallic platinum. Instead of in this way deducing by calculation the weight of metallic platinum from that of the double salt obtained, its amount may be at once determined by first expelling the ammoniacal salts, and afterwards weighing the metallic spongy platinum which remains.

For this purpose the double chloride should be exposed to a full red heat in a closed porcelain crucible, protected from the direct action of the fire by being enclosed in an ordinary earthen pot : the decomposition of this salt may likewise be effected by the flame of a gas-burner or spirit-lamp, and in that case the external crucible of fire-clay must not be employed. This decomposition of the double salt by heat requires to be conducted with great care, since if the evolution of ammoniacal gas be too rapid, a notable amount of metallic platinum will be carried off by the evolved gases. Instead of using chloride of potassium may be employed; the double chloride of platinum and potassium which is in this case produced is either dried and weighed, as when chloride of ammonium has been employed, or decomposed, by heating to

### PLATINUM.

redness, into metallic platinum and chloride of potassium. The latter is separated by solution and washing in hot water, and the former dried and weighed in the metallic state.

The separation of platinum from other metals is often effected through the insolubility of its double chlorides, deposited on the addition of chlorine of ammonium, or chloride of potassium, to solutions containing chloride of platinum.

The total insolubility of this metal in all the acids excepting nitro-hydrochloric and others capable of liberating chlorine, is another property which frequently affords a ready means of separating platinum from other bodies. From many of the metals platinum is separated in the form of sulphide, by a current of sulphuretted hydrogen gas, by which its precipitation even in acid solutions is completely determined.

When platinum is alloyed with a considerable proportion of any metal soluble in nitric acid, it becomes itself attacked by that reagent, and consequently, although pure platinum is untouched when thus treated, many of its alloys are completely soluble in this menstruum.

From gold, platinum may be separated by dissolving the alloy in aqua regia, and subsequently precipitating the platinum by solution of sal-ammoniac, as above described. The filtrate from the double salt contains the whole of the gold, which may now be precipitated in the metallic state by the addition of protosulphate of iron to the solution.

The pulverulent gold, after being thoroughly washed, is dried, heated, and weighed.

Platinum and silver, when forming an alloy, may be separated by solution in nitric acid, and subsequently precipitating the silver as chloride, by the addition of an excess of hydrochloric acid to the liquor. If a large excess of silver be present, the separation is best affected by the use of sulphuric acid, which dissolves the silver and leaves the platinum in the metallic form.

An alloy of gold, platinum, and silver, may be analysed by solution in nitric acid, which dissolves the silver and platinum, and leaves the gold untouched. The silver is now separated in the form of chloride by the addition of hydrochloric acid, and the platinum precipitated from the filtrate, by the addition of chloride of ammonium, by which the formation and precipitation of the double platinum salt is determined.

Platinum and copper may be separated by dissolving the alloy in aqua regia, and afterwards precipitating the metallic platinum by a bar of pure copper. The separation of these metals is also readily obtained by means of sulphuric acid, by which the copper is dissolved, whilst the platinum remains as a metallic powder.

An alloy of platinum with gold, silver, and copper, may be analysed as follows :- The alloy is dissolved in aqua regia, and the liquor copiously diluted with distilled water. The solution is now separated from a flocculent precipitate of chloride of silver by filtration. The chloride thus obtained may be either fused, and its equivalent in metallic silver determined by calculation, or it may be reduced by boiling with zinc and sulphuric acid, when the deposited silver is washed, dried, and weighed. The filtrate obtained from this precipitate is now concentrated, and mixed with an excess of alcohol: sal-ammoniac is subsequently added, and from the weight of the precipitate obtained is calculated the amount of platinum originally present. To the solution filtered from the platinum deposit is added a solution of protosulphate of iron, together with a few globules of metallic mercury. The flask containing the mixture is gently heated, and afterwards briskly shaken, in order that the precipitated gold may become completely amalgamated. The amalgam thus obtained is first carefully washed and dried, and afterwards heated in a porcelain crucible, until the whole of the mercury has been expelled, and the gold alone remains in the metallic state. The weight of copper present may be estimated by difference, and represents the loss sustained on deducting from the total amount of alloy operated on, the united weights of gold, platinum, and silver found.

The ores of platinum cannot be assayed in the dry way, and their complete analysis is a long and difficult operation, which can only be successfully undertaken by an experienced chemist. The commercial assay of platinum ores is best conducted by carefully performing on a small scale the various operations now to be described.

## METALLURGY OF PLATINUM.

The platiniferous sands subjected to metallurgic treatment, besides containing the principal metal sought, also yields variable quantities of the constantly associated metals, palladium, osmium, iridium, rhodium, and ruthenium; they also frequently contain, in addition to these, gold, silver, iron, and copper, together with various heavy minerals, such as titaniferous and chrome iron ores.

When gold is present in sufficient quantity, the ore is first subjected to amalgamation for the purpose of its extraction, and the residue, after a careful mechanical preparation, is subsequently treated for the platinum which it contains. The mineral thus concentrated by washing is attacked by aqua regia, containing an excess of hydrochloric acid, in large green glass carboys, which

#### PLATINUM.

are heated on a sand-bath placed under a lofty chimney, by which the evolved fumes are rapidly carried off. The aqua regia by which the attack is made, is always diluted by a little distilled water, as by this means a smaller quantity of iridium is dissolved than when the acids are employed in an undiluted state, and when this metal is present even in small quantity the platinum produced is rendered extremely hard and brittle. The aqua regia is removed several times before the solution of the ore is completed, and great care is taken to avoid the inhalation of the escaping fumes, which, from the presence of osmic acid, are extremely prejudicial to the workmen. The solution thus obtained is now set aside, in order that it may brighten by precipitation, and the clear liquid, after being drawn off by a glass syphon, is treated with a solution of sal-ammoniac as long as a vellow precipitate is deposited. The mother liquors from this precipitate still contain a considerable amount of platinum, together with variable quantities of the other metals originally present in the ore; these are precipitated by bars either of zinc or iron, by which a deposit of a dark colour is produced, from which a certain amount of platinum is obtained. With this view the dark deposit is first treated with hydrochloric acid, by which the foreign metals are principally dissolved, and the residue subsequently re-attacked by highly diluted aqua regia, which readily dissolves the finely divided platinum, without acting in a sensible degree on the iridium which the mixture contains. Sal-ammoniac is now added to the clear solution, and a second precipitate of the double chloride of platinum and ammonium obtained.

The double chloride thus procured is heated to dull redness in large wrought iron crucibles, and by this means the ammoniacal salts are expelled, whilst metallic platinum in a spongy state remains.

This spongy platinum is next finely pulverised, by being rubbed between the hands, and afterwards intimately mixed with water, so as to form a dense black slime. This is carefully passed through sieves of extremely fine wire gauze, and the coarser particles which remain on the meshes again crushed, and ultimately made to pass through them.

In conducting this operation, it is of the greatest importance to avoid the use of any hard body, by which a commencement of aggregation between the particles of metal is produced : the most scrupulous cleanliness on the part of the workmen is also necessary, to prevent the introduction of any extraneous matter into the finely divided mass, as the presence of a hair, or any small dust, would be quite sufficient to cause a serious imperfection in the forged platinum produced. For this purpose the metallic powder is separately washed by decantation, previous to its consolidation into one mass.

The platinum paste is now introduced in an apparatus consisting of a large gun-metal cylinder, accurately fitted with a steel piston, and enclosed at the lower end in a steel foot-piece, by which the escape of the pasty mass is effectually prevented. Great care is also taken that the mass to be compressed be entirely free from air-bubbles, and after first ramming with a wooden pestle, the steel piston is applied. The water is thus separated from the metallic particles, and their closer compression is afterwards effected in an hydraulic press. The discs of platinum thus formed are subsequently heated to whiteness in earthen crucibles, and then beaten on an anvil with a heavy hammer, until a perfectly homogeneous mass has been obtained.

Platinum admits of being forged and welded like wrought iron, and is extensively employed in the manufacture of chemical instruments, and for the negative element in galvanic batteries. Large platinum vessels are likewise used by gold refiners, and platinum stills, for the concentration of sulphuric acid, have at the present day almost entirely superseded those of blown glass.

The other metals contained in the ores of platinum are seldom applied to useful purposes, but palladium is occasionally used for making the divided limbs of astronomical instruments, and rhodium and iridium have sometimes been employed for giving hardness to the points of metallic pens.

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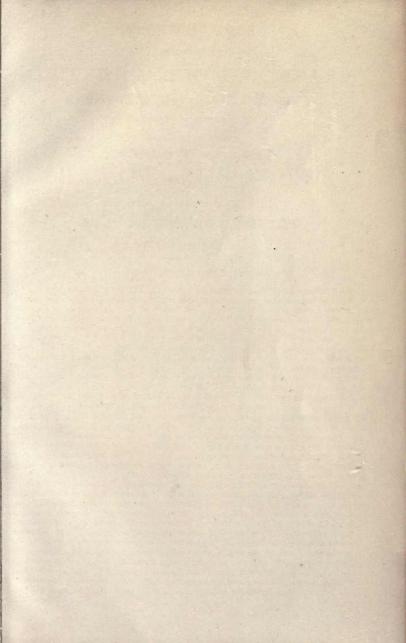
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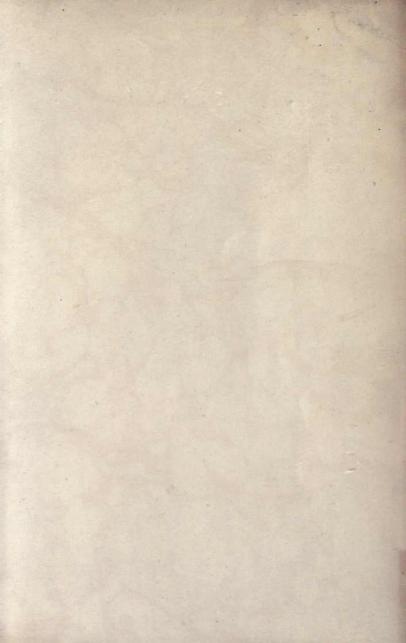
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