gold 514·0 parts per thousand, and silver 75·8 parts per thousand, and its value was reckoned at £1028. The value, however, as calculated from the mean of fourteen assays on the ingot was only £965. In the case of gold and zinc Matthey found that the gold tends to liquate towards the centre of the mass, but only slightly.

An alloy containing 900 parts of gold and 100 of zinc in the form of a sphere 3 in. in diameter was found to be only 1 to $2\frac{1}{2}$ parts per thousand richer in the centre than at the outside. Lead behaves in a similar manner; but the liquation is more marked, the centre of a sphere containing 30 per cent. of lead being 29 parts per thousand richer than the outside. When both lead and zinc are present the liquation is still more marked, and in the case of an alloy containing 15 per cent. of lead and 10 per cent. of zinc the sphere contained 657 parts per thousand at the top, 785 in the centre, and 790 at the bottom. In connection with these alloys it is a curious fact that if the quantity of silver present is not less than two-thirds that of the lead and zinc together, they show very little tendency to liquate, and an alloy containing 55 per cent. gold, 7 per cent. zinc, 18 per cent. lead, and 20 per cent. silver, was found to be practically homogeneous.

CHAPTER III.

METHODS OF INVESTIGATION.

THE experimental difficulties encountered in any attempt to inquire into the nature and constitution of metals and alloys are by no means inconsiderable, and until comparatively recently the subject has been one for speculation and hypothesis rather than for any positive knowledge. These difficulties, however, have been largely overcome by the improved methods of modern research, and before dealing with the constitution of alloys it may be well to consider the various methods which have been employed in their investigation.

These have been conveniently classified by Roberts-Austen and Stansfield under the following heads :—

1. The Chemical Grouping of the Metals in a Solid Alloy.
2. The Separation of the Constituents during Solidification.

The first of these includes the following methods of investigation :—

 a. The specific gravity of alloys.
 b. The electrical resistance of alloys.
 c. Diffusion of metals in alloys.
 d. Electrolytic conduction.
 e. Thermo-electric power.
 f. The heat of combination of metals to form alloys.
 g. The electromotive force of solution of metals and alloys.
 h. Isolation of the constituents of alloys by chemical methods.
 i. Microscopical examination of alloys.

The second group deals with those methods involving a study of the separation of the constituents of an alloy on solidification, and includes—

(*a*) Measurement of fall of temperature during solidification by means of a pyrometer.

(*b*) Mechanical separation of the constituents of an alloy by heating to definite temperatures, and draining off or pressing out the liquid portion.

(*c*) Investigation of the changes in the magnetic character of certain alloys during heating and cooling.

The first four of these methods, viz. the determination of specific gravity, electrical resistance, diffusion and electrolytic conduction, have already been considered under the "Properties of Alloys," and need not be dealt with here.

Thermo-electric Power.—This property has been suggested as a means of throwing light on the nature of alloys, but has not been very fruitful in results, owing to the fact that a change in thermo-electric power may be caused by an allotropic as well as a chemical change.

The Heat of Combination of Metals to form Alloys.—A great many metals evolve heat when united, such as aluminium and copper, platinum and tin, arsenic and antimony, bismuth and lead; while the union of others, such as lead and tin, is accompanied by an absorption of heat. In this case the absorption of heat is small; but there is an example of an alloy, first described by Mohr, in which a very marked lowering of temperature can be produced. This alloy is formed by taking finely divided tin, lead, and bismuth in their equivalent proportions and rapidly mixing them with eight equivalents of mercury. In this way the temperature of the mixture will actually fall from $+17°$ to $-10°$ C. The determination of the heat of combination may be made by adding one metal to another in the molten state; but in the case of solid alloys the determination can only be arrived at by indirect methods. One such method consists in comparing the heats of solution of the alloy and of the separate metals in acids; but this method is open to objections. Lord Kelvin, Galt, and Gladstone have made determinations of the heat of combination; but, so far, the results have not added much to our knowledge of the constitution of alloys.

Baker (*Phil. Trans.*, vol. cxcvi. p. 529) has made determinations of the heat of combination of a large number of copper alloys. The method adopted consists in determining the difference between

the heats of dissolution of the alloy and an equivalent weight of its constituents in a suitable solvent. The solvents employed were an aqueous solution of chlorine, a mixture of ammonium and ferric chlorides, and a mixture of ammonium and cupric chlorides.

In the case of the copper-zinc alloys the experiments show that—

1. There is an evolution of heat in the formation of all the alloys.

2. This evolution of heat reaches a maximum in the case of the alloy corresponding to the formula $CuZn_2$ (*i.e.* 32 per cent. of copper).

The Electromotive Force of Solution of Metals and Alloys.—This method has been used by Laurie, and has given most valuable evidence as to the existence of compounds in alloys. The method, as employed by Laurie, depends upon the fact that if in a galvanic cell—say, for example, a Daniell cell—the zinc plate is replaced by a compound plate made by joining together rods or plates of copper and zinc, the electromotive force is not altered; this is the case even if the zinc surface is only one thousandth part of the copper surface. If now the zinc plate in a Daniell cell is replaced by zinc alloys containing increasingly large percentages of copper, it is found that the electromotive force does not vary appreciably until an alloy containing 33 per cent. of copper is reached, when there is a sudden fall in the electromotive force. From this it is argued that in this alloy there is no free zinc present; but that it is all in combination with the copper, and forms an alloy which may be represented by the formula $CuZn_2$. In the same way with the copper-tin alloys, a sudden change in the electromotive force is noticed when the composition of the alloy corresponds to a formula $SnCu_3$. Moreover, if an alloy containing an excess of tin be employed the excess of tin is dissolved out until the same alloy $SnCu_3$ is reached, when no further change occurs. These results bear out the evidence obtained from the determinations of the density, thermal and electrical conductivity, and also the microscopical examination and cooling curves. These will be discussed later.

Isolation of the Constituents of Alloys by Chemical Means.—It frequently happens that one constituent of an alloy is less soluble in a given solvent than the remainder of the alloy, and

this is more especially the case when compounds are present. It is therefore possible, by using a suitable solvent, to dissolve away the more soluble portion, and this can often be facilitated by the employment of an electric current. The residue can then be filtered off and analysed. Photograph 4 is an example of a compound separated in this way.

The Microscopical Examination of Alloys.—The evidence afforded by the microscope, in relation to the constitution of alloys, has been of such value that it may with advantage be considered at some length.

The systematic study of the structure of metals as revealed by the microscope was first undertaken by Dr Sorby of Sheffield as an introduction to the study of meteoric irons. "It was a natural thing," he says, "that I should be led from the study of the microscopical structure of rocks to that of meteorites, and in order to explain the structure of meteoric iron I commenced the study of artificial irons." He began this study in 1863, and in the following year his paper *On a New Method of Illustrating the Structure of various Kinds of Steel by Nature Printing* was published by the Sheffield Literary and Philosophical Society. In 1865 his paper *On the Microscopical Structure of Meteorites and Meteoric Iron* was published by the Royal Society. Nothing further appears to have been done until Prof. Martens published in 1878 the results of his investigations, which were carried out quite independently. The importance of the study of the microstructure of metals and alloys was soon recognised, and the work of Dr Sorby and Prof. Martens was taken up and extended by Wedding, Osmond, Andrews, Behrens, Howe, Charpy, Le Chatelier, Roberts-Austen, Stead, and many others.

In order to study the structure of a metal or alloy by means of the microscope it is first necessary to prepare a polished surface, and for this purpose a section of convenient size must be obtained. In the case of comparatively soft alloys this may be effected by sawing through the alloy with a hack saw and then filing into shape. In the case of hard and brittle alloys a diamond cutter may be used, but a simpler method consists in breaking the alloy and selecting a fragment with a comparatively smooth face. This face is then ground down on an emery wheel until flat. The section is now rubbed down on emery papers of increasing fine-

ness, using first the ordinary English papers and then those of French make used by steel engravers, and marked 0 to 0000. The grinding on each paper must be continued until the scratches produced by the previous paper have entirely disappeared, when the next paper is substituted and the section turned through an angle of 90°, so that the new scratches are at right angles to the previous ones. In this way it is easy to see when the coarser scratches have disappeared. This preliminary polishing is most rapidly performed by attaching the emery papers to the surfaces of wooden blocks or wheels, which are made to revolve at a high rate of speed. After rubbing down on the last emery paper the surface should be free from all coarse scratches, and is now ready for the final polishing. Various methods have been devised by different workers for the final polishing of the section, and some of these will now be dealt with.

For rough work the section may be polished on a wheel covered with chamois leather or broadcloth, upon which a small quantity of fine dry jeweller's rouge has been sprinkled. For finer work the wheel should be covered with broadcloth which is kept wet, and well-washed rouge employed. Wet polishing may take longer, but is far more satisfactory than dry.

Rouge suitable for polishing is prepared in the following way: A quantity of jeweller's rouge is stirred up with a large bulk of water (about 50 grams of rouge to a litre of water) in a large jar or beaker, and is then allowed to stand for thirty seconds and the liquid decanted. This is allowed to stand for some time, when the water is poured off, and the rouge which has settled is used for the polishing.

With some alloys it is well to avoid the presence of water, and in these cases the rouge may be moistened with a little paraffin. This method is very successful in the case of copper and copper alloys.

Le Chatelier has made a number of experiments on the subject of polishing, with a view to increasing the speed of the manipulation. He points out that in the washing of powders the quantity of carbonate of lime in the water is quite sufficient to cause the formation of lumps, containing both coarse and fine particles, and he recommends the following method :—The powder is first treated with water containing one part of nitric acid in one

thousand of water, in order to dissolve any salts present. The mixture is stirred, allowed to settle, and the clear liquid decanted. The process of washing and decanting is now continued with distilled water until the acid is removed and the settling takes place more slowly. The separation of the powder is then effected by adding two cubic centimetres of ammonia to each litre of water, and the top portion of the liquid is syphoned off at intervals of fifteen minutes, one hour, four hours, twenty-four hours, and eight days. After the removal of the twenty-four-hours powder the finer particles still in suspension may be caused to settle rapidly by adding a small quantity of acetic acid to the liquid.

The powder in the first deposit is unsuitable for polishing, and the second and third are somewhat coarse, but the deposits collected between the first and the eighth day constitute the true polishing powders.

The powders so prepared are mixed while still wet with thin shavings of very dry Castile soap, in the proportion of one part of dry soap to ten parts of the wet powder. The mixture is melted in a water bath and allowed to cool, stirring continuously, until the mass begins to thicken; it is then poured into tin tubes similar to those in which oil paints are kept.

Le Chatelier has found the following substances to be the most satisfactory:—Alumina obtained from the calcination of ammonia alum, commercial flour emery, oxide of chromium obtained from the calcination of ammonium bichromate, and oxide of iron obtained from the calcination of iron oxalate. Alumina gives far better results than the others.

These are the usual methods for obtaining a polished surface; but when soft metals have to be dealt with, such as lead, it is extremely difficult to obtain a good polish, and only the slightest pressure must be used. To overcome this difficulty Ewing and Rosenhain have adopted a method of obtaining a smooth surface without having recourse to any mechanical polishing. This method is especially useful in the case of research work carried out on easily fusible metals and alloys, and consists in pouring the molten metal on to a smooth surface such as glass, mica, or polished steel, in contact with which it is allowed to solidify. In practical work, however, it is obviously not permissible to melt the alloy, and the specimen must be polished. For this purpose

a little Globe metal polish and chamois leather will be found quite as satisfactory as more elaborate methods.

When an alloy which is composed of constituents of different degrees of hardness is polished on a soft material, such as leather, cloth, or parchment, the hard constituents will appear in relief, and a preliminary examination of the polished surface is frequently of great value in affording information as to the relative hardness of the constituents of an alloy. As a rule, however, it is necessary to subject the polished surface to the corroding action of some chemical reagent in order to distinguish the constituents. This process is known as "etching." The reagents most frequently used are the various acids, but alkalis, alkaline sulphides, and many other reagents are also used, either in aqueous or alcoholic solutions. Some alloys are most satisfactorily etched by placing the polished specimen in a salt solution and connecting it with the positive pole of a battery, while the negative pole is connected with a piece of platinum foil.

In addition to the ordinary methods of etching there is the method of "heat tinting," which consists in simply heating the specimen in air until the polished surface assumes a decided colour due to slight oxidation, and then cooling quickly by floating on mercury. This method has proved of the greatest value in the hands of Mr Stead, who has shown that it is the only satisfactory method by which carbide and phosphide of iron can be distinguished when associated in iron. It is usually sufficient to heat the specimen on a hot plate, but if any definite temperature is desired a bath of molten tin or lead may be employed. Modifications of this method consist in heating the specimen in gases, such as sulphuretted hydrogen, in order to obtain a film of sulphide or other compound in place of the oxide.

The methods of etching are so numerous that it is impossible to deal with them except in a general way, but an attempt will be made to indicate the most satisfactory methods for the various alloys in the chapters dealing with them.

The complete microscopical examination of a metal or alloy should be carried out in three stages. First, the specimen should be simply polished and examined under both low and high powers. This will afford information as to the relative hardness of the constituents, and will also reveal the presence of blowholes, cracks,

and included foreign matter, such as slag, cinder, or unalloyed metal. The second examination should be made after slightly etching the polished surface in order to distinguish the constituents. This is the most difficult part of the whole process, and great care should be taken not to overdo the etching. The safest method is to etch very lightly and examine; then etch a little further and again examine, and continue the etching until the separate constituents are clearly shown. For the third examination the specimen should be deeply etched with a stronger reagent in order to show up the crystalline structure of the metal. The first and third examinations can usually be carried out with comparatively low magnifications, but the second often requires magnifications of a thousand diameters or more to resolve an alloy into its components.

If it is desired to preserve the specimens for future reference they may either be oiled or the polished surface moistened with a solution of paraffin wax in benzol. This leaves, on drying, a thin film of paraffin which can easily be removed when the specimen is required for re-examination, by wiping with a cloth moistened with benzol. Le Chatelier recommends the use of a solution of guncotton in amyl acetate, which leaves a thin film of transparent varnish. This film does not interfere in the least with the examination of the specimen even under the highest powers.

When the specimen has been prepared it requires to be mounted in order to place it on the stage of the microscope, and this mounting requires a little care in order that the surface may be at right angles to the optical axis of the microscope. With a little practice this difficulty can be readily overcome; but one or two mechanical devices for ensuring a perfectly level surface may be briefly described. The simplest of these merely consists of a number of short lengths of brass tube of different diameters which have been carefully cut so that their ends are perfectly true. The specimen to be examined is placed on a glass slip, with the polished surface downwards, and a brass tube is selected which will just pass over the specimen. A quantity of clay or soft wax is then pressed into the tube containing the specimen until it more than fills the tube, and then a glass slip is placed on the top and pressed into contact with the brass ring. Another device has been placed upon the market, and is shown in fig. 5.

This consists of two horizontal plates, the upper one being capable of vertical movement, but always remaining parallel to the lower one. The specimen is placed with its polished surface on the lower plate, and the upper plate, carrying a glass slip to which some suitable clay or wax is attached, is lowered into con-
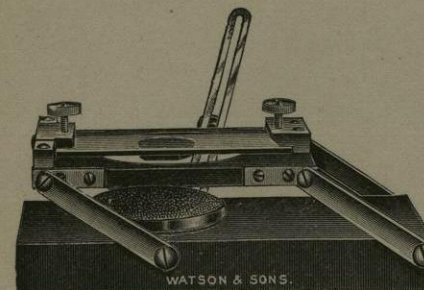

Fig. 5.—Levelling Device for Micro-Sections.

tact. If necessary it can be clamped in position until the mounting medium has set.

To obviate the necessity for mounting the specimen several convenient metal-holders have been devised. Fig. 6 is a simple form of metal-holder, consisting of a metal strip with a raised centre in which there is an aperture. The specimen is held with
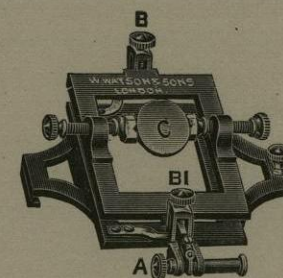

Fig. 6.—Simple Metal-holder for Specimens.

Fig. 7.—Combined Metal-holder and Levelling Device.

the polished surface against the under side of the aperture by means of elastic bands.

Fig. 7 shows a combined metal-holder and levelling arrangement. The specimen is held by two rotating jaws, and can be levelled by means of the screws A and B B1.

It is obvious that the examination of metals must be con-

ducted by reflected light, and the illumination may be either
oblique or vertical. Oblique illumination is only possible with
low powers, and for this purpose natural illumination is some-
times sufficient. In most cases, however, a parabolic reflector is
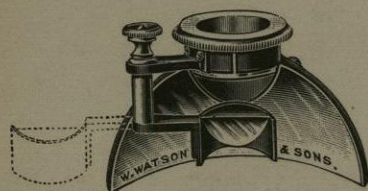desirable, if not necessary. A convenient form of reflector is

Fig. 8.—Sorby-Beck Illuminator.   Fig. 9.—Mirror Illuminator.

that known as the Sorby-Beck reflector, and shown in fig. 8. It
is made to fit on to the objective, and is also supplied with a
small vertical reflector which can be instantly placed in position
or dispensed with by a turn of the screw.

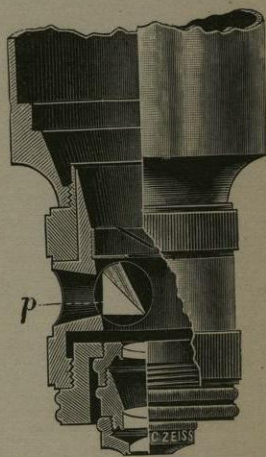For high-power work the illuminator must be placed behind

Fig. 10.—Mirror.   Fig. 11.—Prism Illuminator.

the objective, and the reflector in this case may be either a glass
prism or a very thin glass disc placed at 45° to the optic axis.
These two forms of illuminator are shown in figs. 9, 10, and 11.
It is obvious that in the case of the disc reflector only a portion
of the light is utilised, whereas with the prism the whole of the
light is reflected. This may be a distinct advantage when a

powerful source of light is not available. Both illuminators may
be fitted with stops or diaphragms, so that the amount of light
admitted may be varied as desired. These will be found useful
when the section under examination has a brilliantly reflecting
surface, and also when high-power oil-immersion objectives are
being used.

Any form of microscope may be used if it is only desired to
examine specimens; but if photographic records are to be obtained
it is advisable to employ one of the special microscopes which
have been designed for the purpose. These are fitted with
exceptionally wide body tubes in order to minimise the reflections
from the inside of the tube.

The microscope and camera may be used either in a vertical or
horizontal position when moderate magnifications are required,
but when high-power objectives and a long camera extension
are employed the horizontal position becomes a necessity. An
apparatus, therefore, which is intended for any degree of magnifica-
tion should be placed in this position.

As regards the illumination, an electric arc lamp with automatic
feed is perhaps the most satisfactory; but any brilliant light, such
as an incandescent gas lamp, an oxyhydrogen light, acetylene or
Nernst lamp, will give good results. In any case a condenser
should be placed between the light and the reflector to concen-
trate the rays as much as possible.

Le Chatelier recommends a monochromatic light on account
of the chromatic aberration of the objectives, which are never
completely free from this defect. He obtains a suitable light by
passing the rays from a mercury arc lamp in vacuo through a
solution of sulphate of quinine, which only allows the indigo, green,
and yellow rays to pass, and as the green and yellow rays have
little or no action upon an ordinary plate the light may be con-
sidered monochromatic.

For photographic work slow plates should be used, whenever
possible, on account of the finer grain which they possess; and
better results can frequently be obtained by employing backed
plates, as halation, or reflection from the back of the plate, is a
common source of trouble in photomicrographic work.

Fig. 12 shows a form of microscope specially made for photo-
graphic work by Zeiss of Jena. It is used in conjunction with a

4

camera in a horizontal position, and focussing is effected by a rod
St connected by a universal joint (Tr) with a small milled head
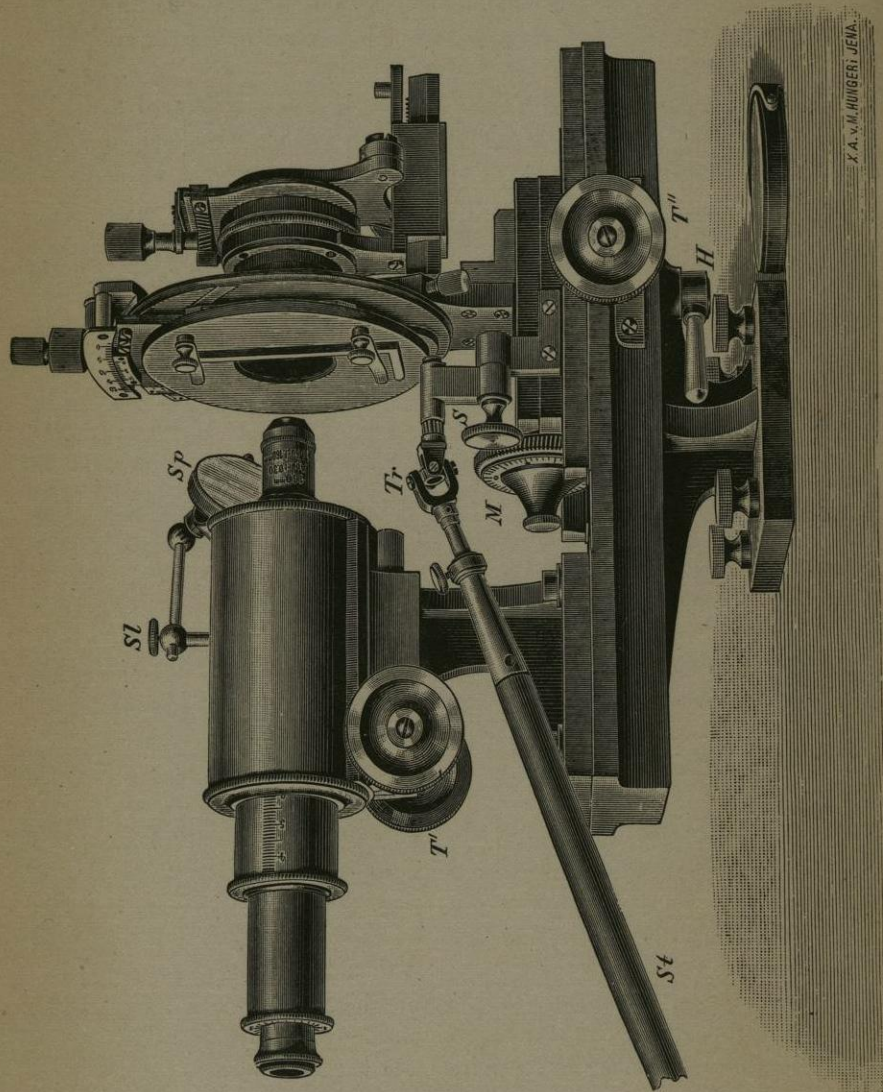which, in its turn, engages the large milled head M.

FIG. 12.—Horizontal Microscope.

The photographs illustrating this book were taken with a
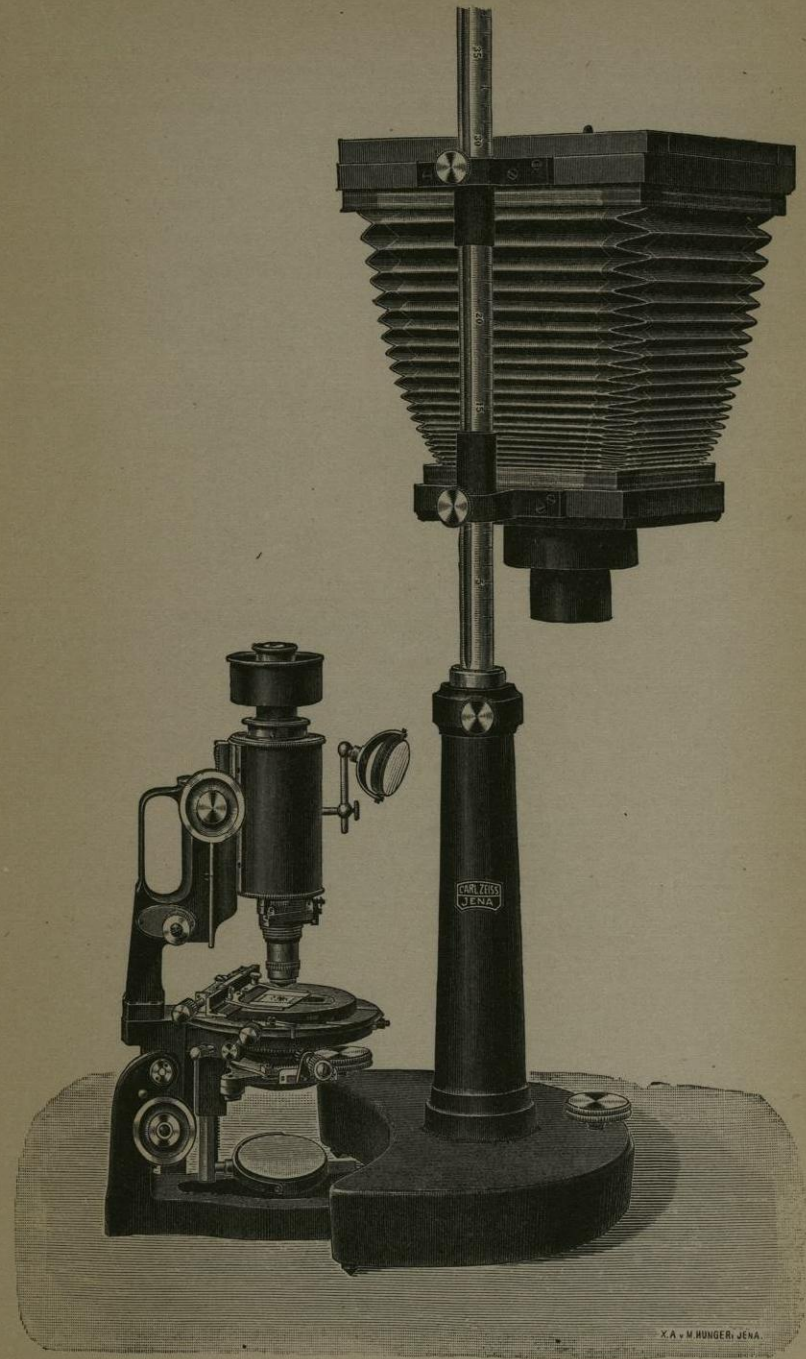microscope of this form which the author has had in constant use

FIG. 13.—Vertical Microscope.

and with perfect satisfaction for the last five years. Fig. 13 illustrates a similar form of microscope intended for use with a simple form of camera in a vertical position.

Fig. 14 is a stereoscopic microscope which has proved useful in the examination of uneven surfaces such as fractures.

Fig. 15 is a micrometer microscope of recent introduction which is likely to prove of great service to the metallurgist. It
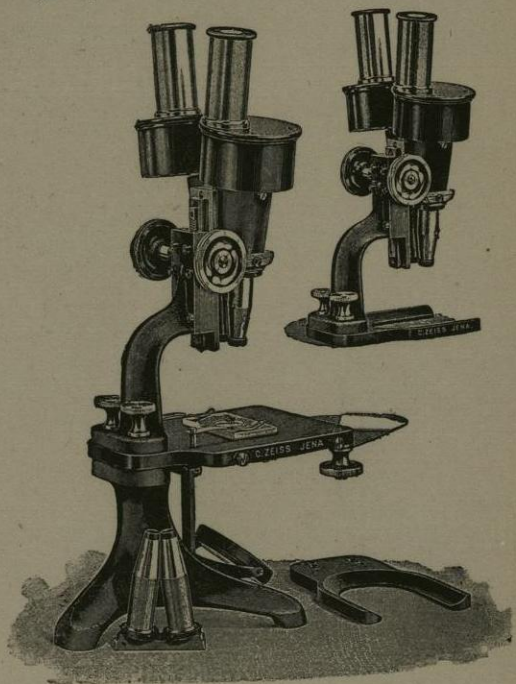

FIG. 14.—Stereoscopic Microscope.

is capable of measuring distances up to 20 mm. with an accuracy of 0·01 mm., and a useful feature of the instrument is that by loosening the screw K the stem of the microscope can be slipped out of the split sleeve H, thus separating the stand from the upper body, which can then be secured by its stem to any laboratory stand and used in any position desired. Another model of this microscope is designed for the measurement of two distances at right angles to each other.

Measurement of Fall of Temperature during Solidification.— In 1884 Dr Guthrie published the results of an investigation

dealing with changes which take place during the solidification of alloys, and he comes to the conclusion that there is a close analogy between the solidification of molten granite and a fluid alloy. Just as, in the case of a mass of molten granite, the quartz and felspar crystallise out leaving the mica still fluid, so in the case of an alloy certain constituents solidify until "the alloy of minimum temperature of fusion" is left behind. This most
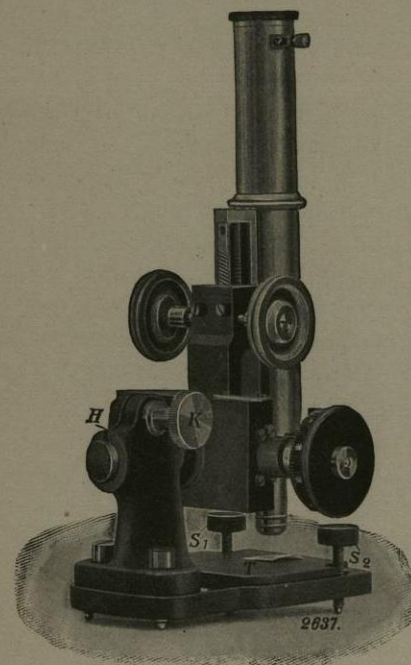

FIG. 15.—Measuring Microscope.

fusible alloy of the series Guthrie calls the *eutectic* alloy, and he points out that the constituents of this alloy are not in simple atomic proportions. "The constitution of eutectic alloys," he says, "is not in the ratio of any simple multiple of their chemical equivalents, but their composition is not on that account less fixed, nor are their properties less definite."

Guthrie was only able to deal with alloys of low melting-point, and, owing to the experimental difficulties involved in the accurate measurement of high temperatures, this method of investigation was practically neglected until the introduction of the Le Chatelier

pyrometer. The study of pyrometry belongs rather to the domain of physics than metallurgy; but the use of pyrometers in the study of alloys has become so important that a brief description of the more useful types may not be out of place.

Pyrometers suitable for the study of alloys, where the temperatures of small masses of metal have to be accurately determined, may be divided into two classes: 1, resistance pyrometers; and 2, thermo-electric pyrometers.

The measurement of temperature by means of the resistance pyrometer depends upon the increase in resistance of a platinum wire when heated. In the Callendar & Griffith's resistance pyrometer a fine platinum wire is wound on a mica frame, which is enclosed in an outer protecting case. The ends of the platinum wire are connected by copper leads either to a direct reading instrument or to a clockwork recorder. In order to avoid the introduction of any error due to the variation of the temperature of the wires connecting the thermometer with the recorder, two similar leads, not connected with the coil, are passed down the whole length of the thermometer. This thermometer may either be connected with a direct reading indicator or an automatic recorder.

The measurement of high temperatures by means of a thermo-electric couple was suggested by Becquerel in 1826; but a satisfactory couple was not obtained until 1887, when Le Chatelier published his researches on the platinum — platinum-rhodium couple. In this apparatus the couple is formed by joining or fusing together the ends of two wires, one of absolutely pure platinum and the other of pure platinum alloyed with 10 per cent. of rhodium. When one junction of these wires is heated an electric current is generated, and this current has been proved, by comparison with the air thermometer of the Royal Physical Institute, to be proportionate to the heat applied. The wires are 0·6 millimetres in diameter, and the current generated is approximately ·001 volt for every hundred degrees Centigrade.

In order to protect the wires from injury they are enclosed in porcelain or fireclay tubes. The Royal Porcelain Factory in Berlin manufacture tubes which will resist a temperature of 1600° C., but a simple fireclay tube is often quite satisfactory. The couple is inserted in the tube with a thin strip of mica between
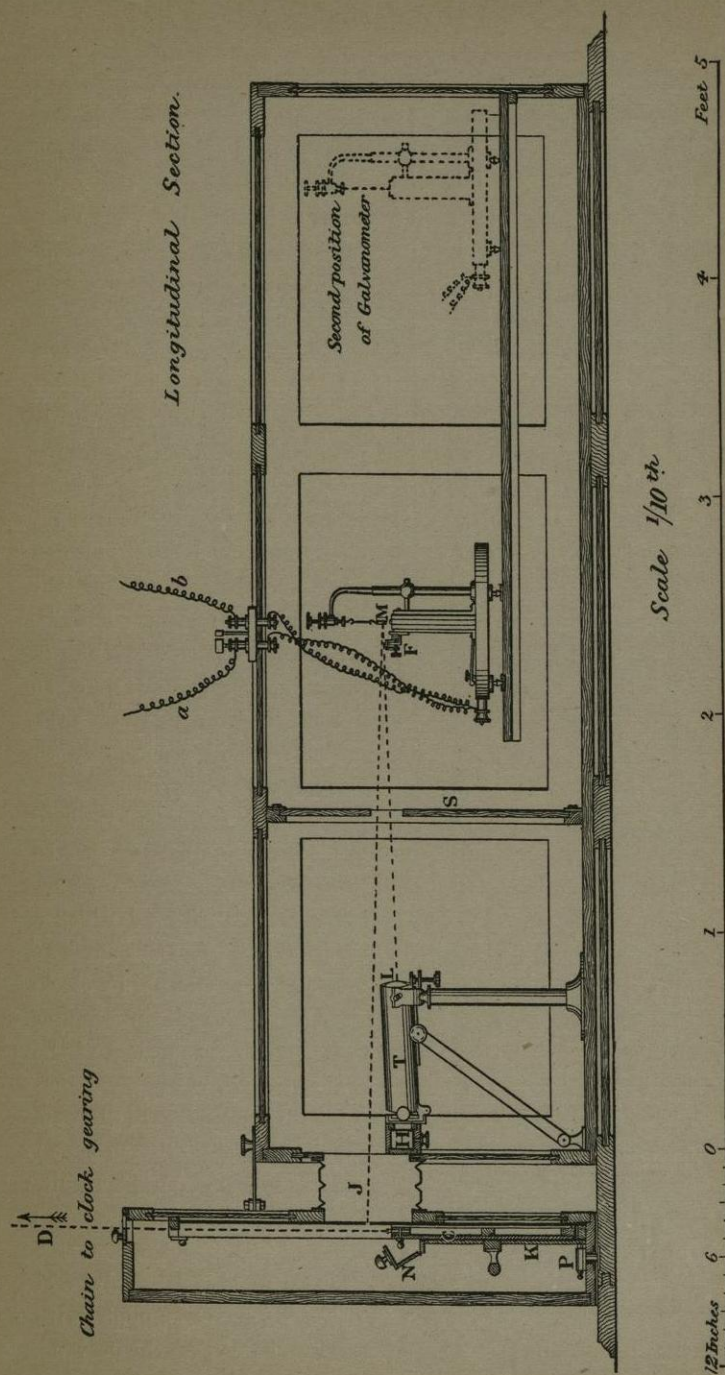

Longitudinal Section.

Second position of Galvanometer.

Chain to clock gearing

Scale 1/10 th.

Fig. 16.—Roberts-Austen's Autographic Recording Pyrometer.

Second position
of Galvanometer

Sectional Plan.

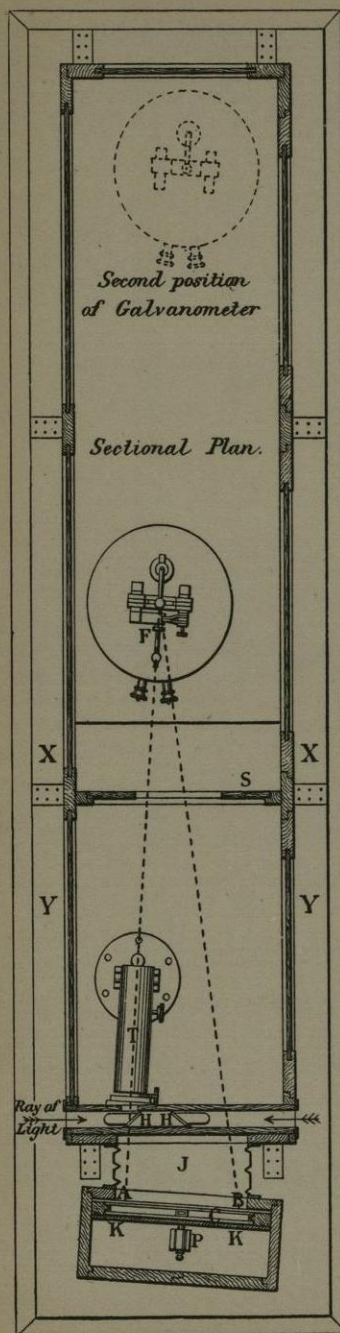X   X

S

Y   Y

Ray of
Light

J

FIG. 16A.—Sectional Plan of Roberts-
Austen's Autographic Recording
Pyrometer.

the wires in order to prevent a short circuit. The other end of the wires forming the couple should be maintained at a constant temperature, if accurate measurements are to be taken ; and to ensure this they are enclosed in glass tubes, which are immersed in ice or else in water whose temperature is accurately known. The thermo-couple measures the difference in temperature between the heated junction and the "cold junction." The copper leads are connected with a galvanometer of the d'Arsonval type, which may be arranged for direct readings or used in conjunction with an automatic recorder. In the automatic recorder devised by Sir William C. Roberts-Austen a mirror galvanometer is used and a beam of light is reflected from the mirror on to a narrow horizontal slit, behind which a photographic plate is caused to move vertically either by clockwork or by means of a water float. The arrangement of the apparatus will be readily understood by reference to fig. 16, which represents the pyrometer used with such admirable results by Roberts-Austen at the Royal Mint.

The camera is about five feet in length and is supplied with three doors, so that the galvano-

meter is accessible for any necessary adjustments. Connected to the camera by a flexible leather bellows is the apparatus which contains the moving photographic plate. F is the galvanometer, which can be placed in one of two positions, according to the range of temperature to be observed. Inside the camera and immediately in front of the photographic plate is the focussing tube T, containing a lens L which receives the light from the mirror H and throws it on to the galvanometer mirror. Any deflection of the galvanometer mirror causes the spot of light to
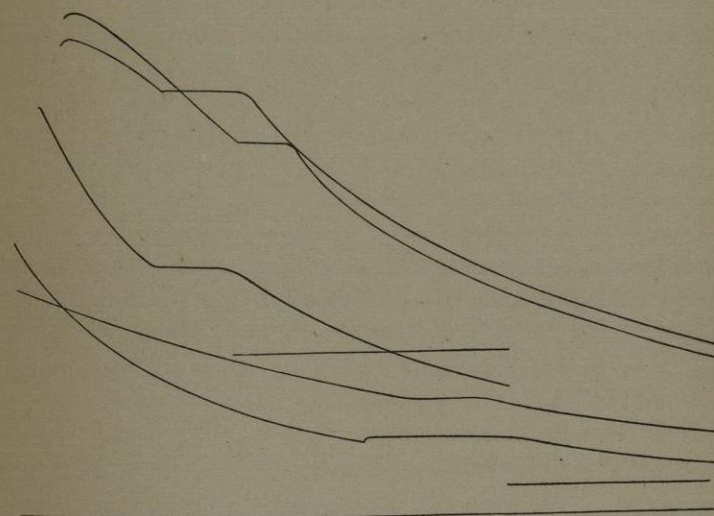

FIG. 17.—Example of Calibration of Pyrometer.

travel along the slit, and thus traces out a curve on the moving photographic plate.

Now it is evident that if the rate of cooling were constant the curve would be the simple resultant of two movements at right angles, and would therefore be a straight line. But the rate of cooling always becomes slower as the body becomes colder, and the actual curve given by a cooling mass is a smooth curve of the form shown in the lower parts of the curves in fig. 17.

If, now, the thermo-couple, suitably protected, is dipped into a mass of pure molten metal—copper, for example—which is then allowed to cool slowly, a different curve is obtained. The

temperature falls steadily until the metal begins to solidify, but at this point the temperature remains constant, owing to the latent heat of fusion of the metal, until the whole of the mass is solid. After this "arrest" in the cooling the temperature falls again in the usual way. The resulting curve, then, is similar to those shown in fig. 17 (which represents the cooling curves of the metals tin, lead, aluminium, silver, and copper, together with two straight lines representing the boiling-points of water and sulphur respectively), and this is a typical cooling curve of a pure metal. There are two possible modifications, however, in the case of pure metals which should be noticed. The first of these is observed when the metal is cooled slowly without being disturbed. Under these conditions the temperature sometimes falls two or three degrees below the true freezing-point of the metal before solidification begins. The freezing of the mass is then accompanied by a sudden rise in temperature to the true freezing-point of the metal. This phenomenon is known as *surfusion,* and it will be remembered that it also occurs in the freezing of water and other liquids. An example of surfusion is seen in the cooling curve of tin in fig. 17, illustrating the method of calibrating a recording pyrometer.

The second modification of the typical cooling curve is not frequently met with, but occurs when a molecular rearrangement takes place in the metal at some temperature below its freezing-point. In other words, the metal at a certain temperature passes from one allotropic modification to another. A molecular change such as this occurs in the case of iron, and is accompanied by an evolution of heat, which is shown in the cooling curve. A further indication of molecular change is shown by the fact that the iron becomes magnetic below this temperature, while before it was non-magnetic. Similar results are obtained in the case of nickel. The magnetic properties of the iron and nickel alloys will be dealt with later.

A number of melting-points of metals have been accurately determined by means of the air thermometer, and these, together with other well-known temperatures, are employed in the calibration of pyrometers. The most useful temperatures for calibration purposes are the following :—

Boiling-point of water	.	.	.	100°
Melting-point of tin	.	.	.	232°
Melting-point of lead	.	.	.	326°
Boiling-point of sulphur	.	.	.	448°
Melting-point of aluminium	.	.	.	657°
Melting-point of silver	.	.	.	961°
Melting-point of copper	.	.	.	1084°

It is absolutely necessary that pure metals be used, and in the case of the boiling-points of water and sulphur the thermo-couple must be placed in the vapour of the boiling liquid and not in the liquid itself. Fig. 17 shows an actual calibration of a Roberts-Austen recording pyrometer. In the first place a "datum" line is taken by letting the photographic plate run while the galvanometer is at rest with no current passing. The plate is then run a second time with the thermo-couple immersed in melted tin contained in a small crucible, and so on, all the curves being taken on one plate. The distances between the datum line and the various points are then measured on the plate, and, if a curve is plotted on squared paper with these distances as abscissæ and temperatures as ordinates, an approximately straight line is obtained from which any other measurement of temperature can be easily read off.

It is advisable that a fresh calibration be made from time to time to ensure that both galvanometer and thermo-couple are in proper working order.

In cases where considerable ranges of temperature have to be measured, a pyrometer, such as that just described, is open to the objection that the large angular deflection of the galvanometer mirror is liable to strain the suspending wires and thus introduce a serious error. To obviate this difficulty the current from the thermo-junction is not allowed to pass directly through the galvanometer, but is opposed by a current from a standard Clark cell, which can be regulated and measured by means of a potentiometer introduced in the circuit. In this way only a portion of the thermo-electric current passes through the galvanometer, and the mirror is only deflected through a small angle. An apparatus of this description, however, requires a special arrangement, as the movement of the spot of light has to be watched and the

electrical balancing of the current carried out during the operation. In this case the galvanometer is not enclosed in a camera, but the room in which the operation is carried out is somewhat darkened, so that the spot of light can be seen travelling along the horizontal slit without fear of fogging the photographic plate.

Sir William C. Roberts-Austen, in his classical researches at the Royal Mint, employed a water clock consisting of a float carrying a photographic plate which moved upwards between guides. The whole was enclosed in a case provided with a horizontal slit, through which the ray of light from the galvanometer mirror might pass. In this apparatus Roberts-Austen introduced a further improvement, by means of which very small
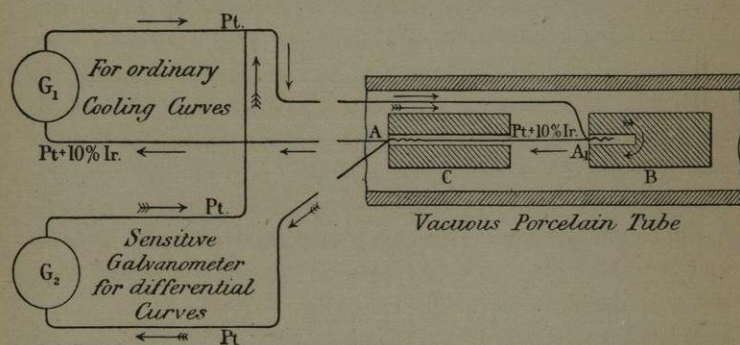

FIG. 18.—Apparatus for Differential Curves.

variations in the temperature of a cooling body could be detected and measured. This method, which has proved to be of the utmost service in metallurgical research, is known as the "differential" method, and the arrangement of the apparatus is shown in the diagram fig. 18.

B is the mass of metal under examination, and A_1 the thermo-couple connected in the ordinary way with the galvanometer G_1. At A, however, a second thermo-junction is formed which is surrounded by a mass of platinum, C, and connected with a second galvanometer, G_2, as shown in the diagram. In this way the first galvanometer measures the actual temperatures, whereas the second only receives such current as may result from the opposing couples A and A_1—that is to say, it measures the difference in temperature between the masses of metal C and B.

Mechanical Separation of the Constituents of an Alloy by Heating to Definite Temperatures and Pressing out the Liquid Portion.—Experiments in this direction are difficult to carry out, but the results are instructive, and serve to confirm the conclusions arrived at by the study of the cooling curves. In 1884 Guthrie described the method and gave some results which he had obtained in the case of alloys with low melting-points. Very little appears to have been done since, but within recent years Roberts-Austen made use of the method in his investigations on the properties of the brasses. The alloy is placed in a steel cylinder provided with two loose plungers, upon which a pressure of about half a ton per square inch is maintained by means of a hydraulic press. The cylinder is gradually heated and the temperature determined by means of a thermo-couple inserted in a small hole drilled in the cylinder. As the temperature rises, a portion of the alloy liquefies and is squeezed out between the plungers; by analysing the extruded portion and noting the temperature at which it became liquid, a very clear idea may be gained of the order in which the constituents of the alloy have solidified and of their approximate compositions.

Change in the Magnetic Character of Alloys during Heating and Cooling.—This method of research is limited to a few alloys, but has been of great service in the case of steels and iron alloys. Iron, nickel, and cobalt are the only metals which possess the property of magnetism at the ordinary temperature, and it is well known that these metals, when heated, lose their magnetism at certain definite temperatures. On cooling they again become magnetic, but usually at a temperature somewhat below that at which they ceased to be magnetic; owing to a resistance to change in the metal, to which the name *hysteresis* has been given. The temperatures at which these metals lose and regain their magnetism are known as the points of transformation, and it is generally supposed that the loss of magnetism is due to an allotropic change in the metal. It is of considerable interest, therefore, to determine the magnetic properties of the alloys of these metals and the influence of other metals on the points of transformation. Some metals raise the point of magnetic transformation; others lower it. Nickel, for example, although itself magnetic, lowers the point of transformation of iron; and an alloy

containing 25 per cent. of nickel requires to be cooled to −50° in order to attain its maximum degree of magnetism.

The magnetic properties of the iron alloys have been studied by Le Chatelier, Osmond, and Mme. Curie, whose original papers should be consulted for further details.

Until recently manganese has been regarded as a non-magnetic metal, but it would seem that it is capable of assuming a magnetic condition when alloyed with other metals. Attention was first called to the fact by Hogg at the meeting of the British Association at Edinburgh in 1892, and his observations have since been confirmed by Heusler and others. The principal magnetic alloys of manganese are those with aluminium, antimony, tin, bismuth, arsenic, and boron.

CHAPTER IV.

THE CONSTITUTION OF ALLOYS.

THE nature and constitution of metals and alloys naturally attracted the attention of the early metallurgists, and Roberts-Austen has pointed out that Achard, Musschenbroek, and Réaumur were all engaged in the study of alloys in the eighteenth century, but it would appear that Boyle was the first to suggest the line of thought which has led to our present views of the constitution of metals and alloys. Discussing the states of matter, he says: "Even such as are solid may respectively have their little atmospheres"; and he adds: "For no man, I think, has yet tried whether glass, and even gold, may not in length of time lose their weight."

Boyle was therefore clearly of the opinion that the solid state of matter was not far removed from, and was in fact usually accompanied by, the liquid or gaseous states, and two hundred years later his belief was proved to be correct by the experiments of Merget and Demarcay.

In 1860 the same suggestion is made by Matthiessen, who, after describing his experiments on the electrical conductivity of alloys, says: "The question now arises, What are alloys? Are they chemical combinations, or a solution of one metal in another, or mechanical mixtures? And to what is the rapid decrement in the conducting power in many cases due? To the first of these questions," he adds, "I think we may answer that most alloys are merely a solution of one metal in the other; that only in a few cases may we assume chemical combinations." Three years later Graham declared his belief that the solid, liquid, and gaseous states probably always co-exist in every solid substance, and he